Advanced solid state physics

Defects in solids

"Defects" in Solids

"Solids are like people - imperfect!

It's the defects that make them unique & interesting"

(J. Corish)

http://www.bath.ac.uk/podcast/powerpoint/Inaugural_lecture_250407.pdf

What you now know

- Metals, many ceramics and some polymers are crystalline
- The atoms re arranged in ordered arrays extending in all directions
- Characterized by a "unit cell", the repeat unit of the array
- Metals have fcc, hcp or bcc crystal structures
- Directions and planes in the crystal are described by Miller or Miller-Bravais (hcp only) indices.

http://www.materials.ac.uk/elearning/matter/crystallography/indexingdirectionsandplanes/indexing-of-hexagonal-systems.html

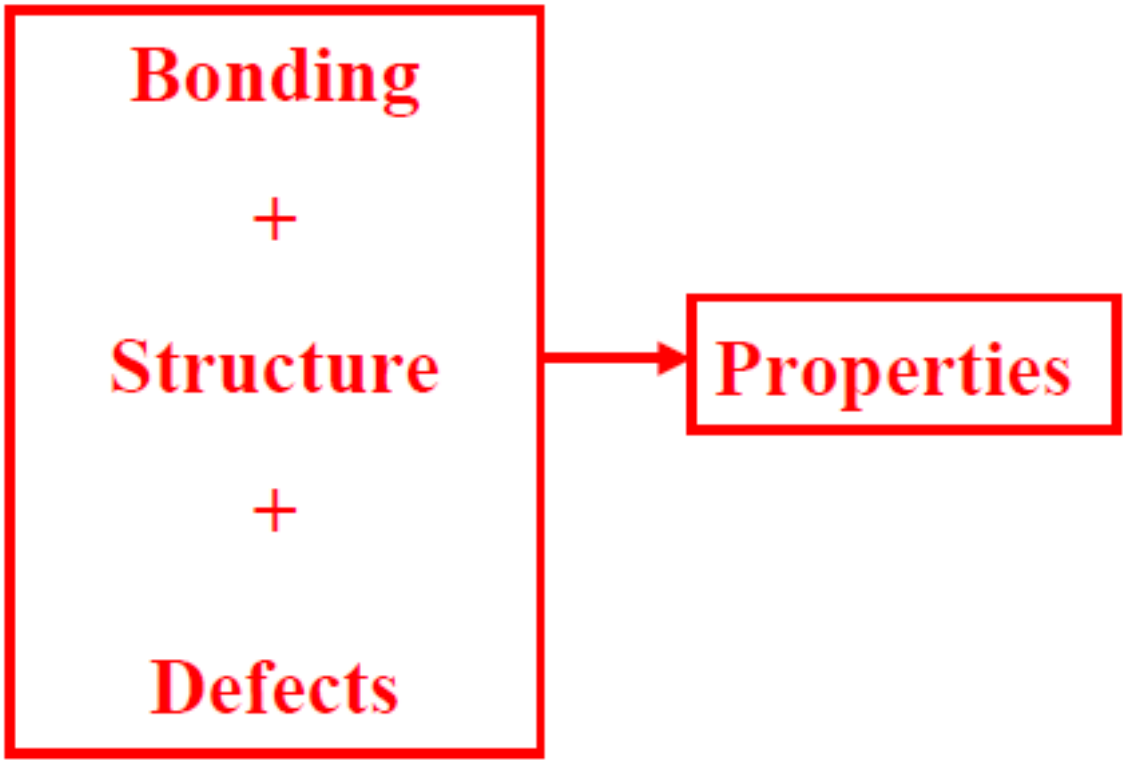
Imperfections in Crystalline Solids

There is no such thing as a perfect crystal.

- Real crystals contain various types of imperfections. We have briefly touched on the fact that many engineering materials are polycrystals
- Many of the important properties of materials are due to the presence of these imperfections

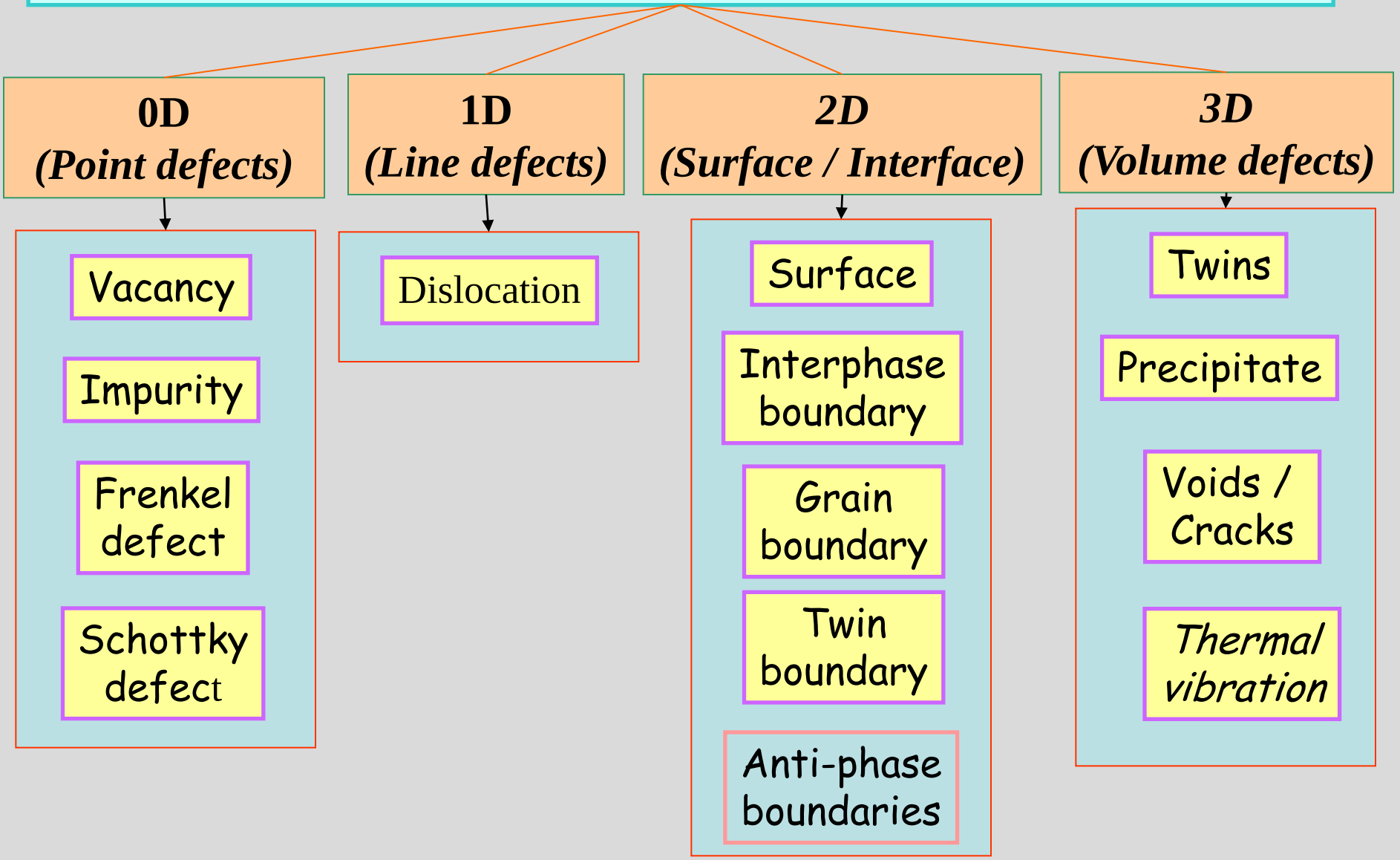
http://www.materials.ac.uk/elearning/matter/crystallography/indexingdirectionsandplanes/indexing-of-hexagonal-systems.html

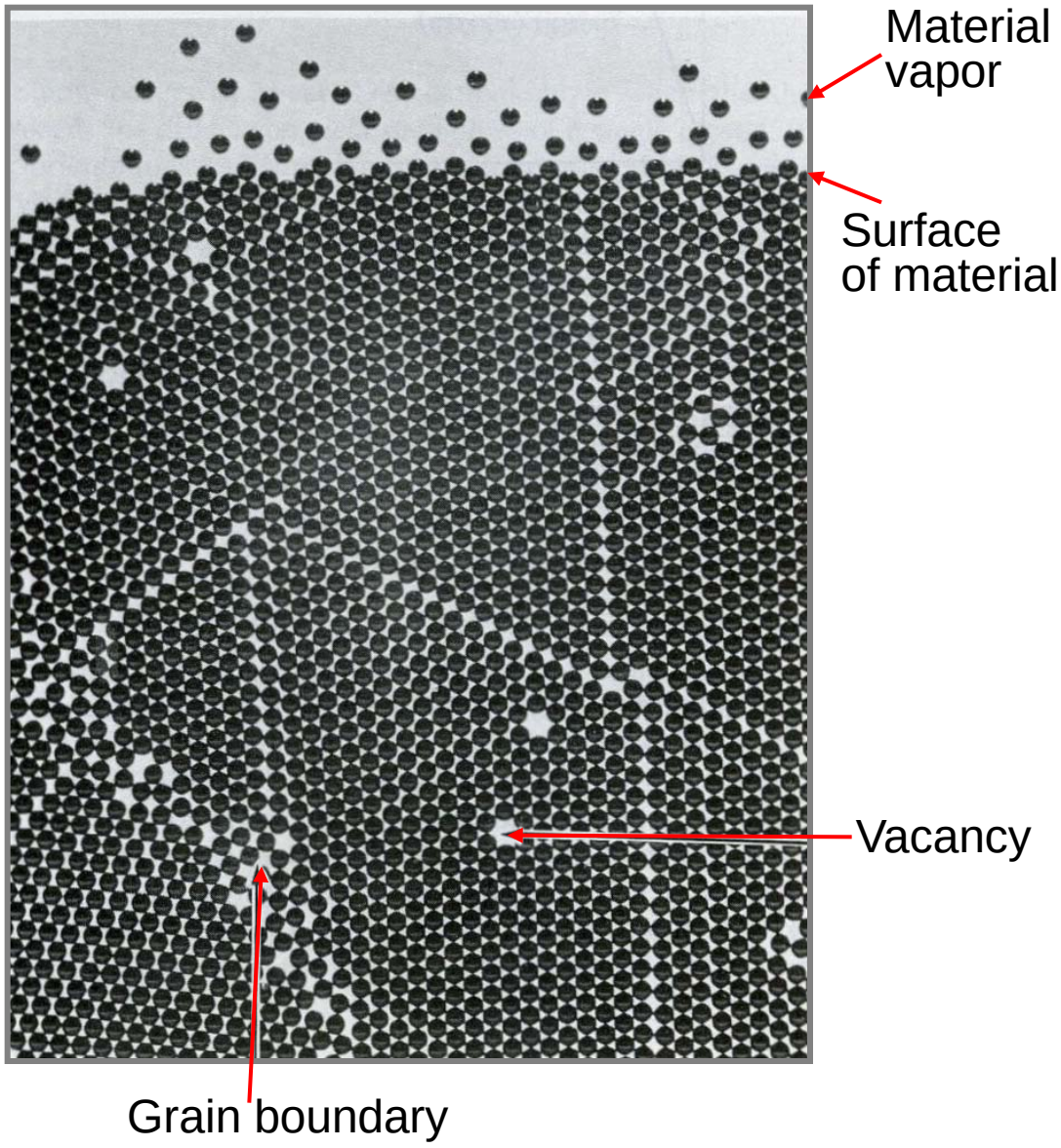
Defects have a profound impact on the macroscopic properties of materials



http://web.utk.edu/~prack/mse201/Chapter%204%20Defects.pdf

CLASSIFICATION OF DEFECTS BASED ON DIMENSIONALITY





Ball bearings can be used to simulate how atoms are packed together in solids.

The photo shows a ball-bearing model set up to show what the grain boundaries look like in a polycrystalline material.

The model also shows up another type of defect-the vacancy-which is caused by a missing atom.

Photograph taken from: Engineering Materials 1: An Introduction to Properties ..., Volume 1 By M. F. Ashby, David Rayner Hunkin Jones, Elsevier 2012.

All solids, even the most 'perfect' crystals contain defects. Defects are of great importance as they can affect properties such as mechanical strength, electrical conductivity, chemical reactivity and corrosion. There are several terms used to describe defects which we must consider:

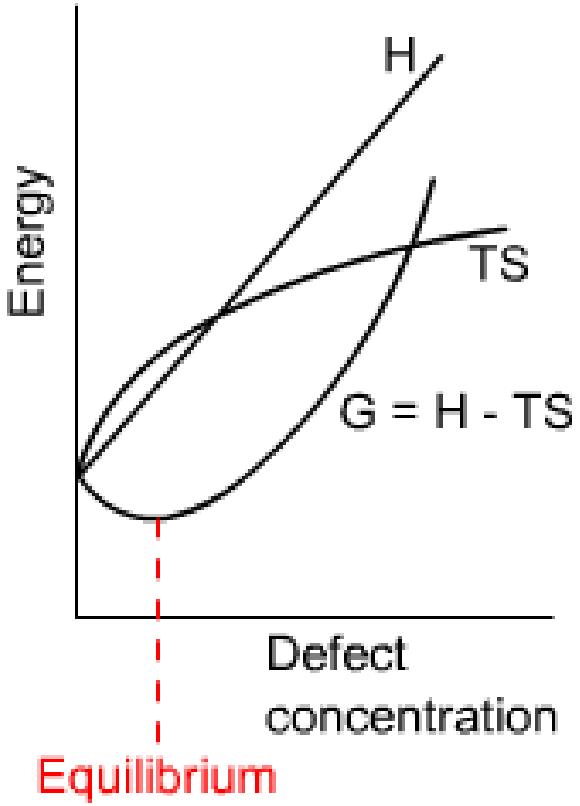
Intrinsic defects – present for thermodynamic reasons.

Extrinsic defects – not required by thermodynamics and can be controlled by purification or synthetic conditions.

Point defects – Occur at single sites. Random errors in a periodic lattice eg absence of atom from usual place (vacancy) or atom in a site not normally occupied (interstitial).

Extended defects – ordered in one, two and three dimensions. Eg errors in the stacking of planes.

Every solid has a thermodynamic tendency to acquire point defects, as they introduce disorder and therefore increase entropy.



The variation of enthalpy and entropy of a crystal with an increasing number of defects. The Gibbs free energy has a minimum at a nonzero concentration. Therefore defect formation is spontaneous.

The Gibbs free energy, G = H – TS, of a solid, is contributed to by the entropy and enthalpy of the sample
Entropy is a measure of disorder within a system, hence, a solid with defects has a higher entropy than a perfect crystal.

https://www.unf.edu/~michael.lufaso/chem4627/ch5_solid_state.pdf

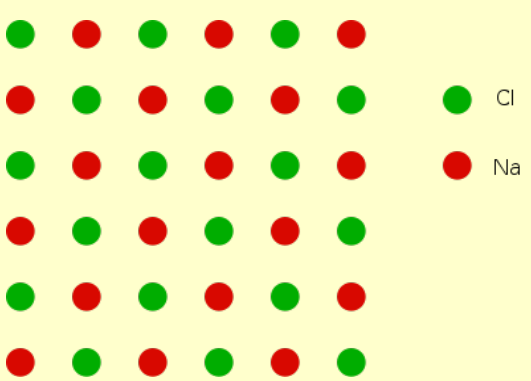
Intrinsic point defects:

Point defects are not easy to directly detect. Several techniques have been used to study them. Two physicists, Frenkel and Schottky used conductivity and density data to identify specific types of point defects.

Schottky defect – Vacancy in an otherwise perfect lattice. Point defect where atom / ion is missing from its usual point in the lattice. Overall stoichiometry usually unaffected as there is normally equal numbers of vacancies at both M and X sites preserving charge balance.

These defects are encountered more commonly when metal ions are able to easily assume multiple oxidation states.

(MX)



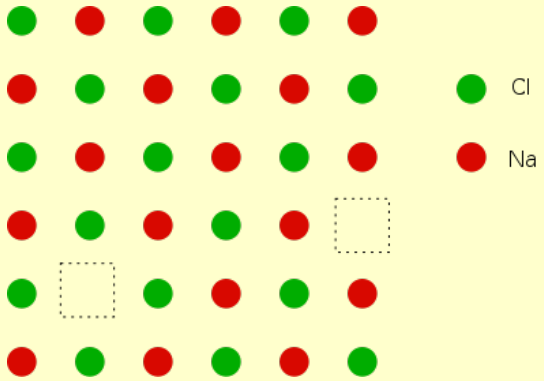
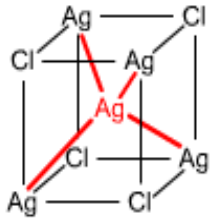
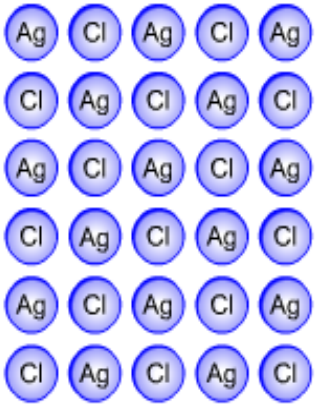


fig. 16



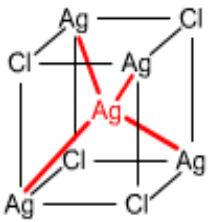
Interstital Ag^+

fig. 17



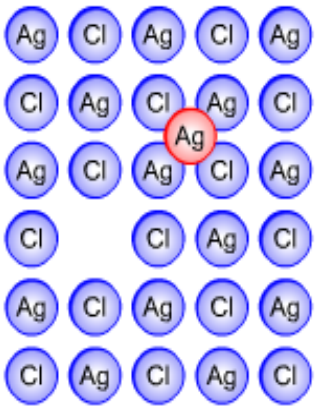
Perfect lattice

fig. 16



Interstital Ag^+

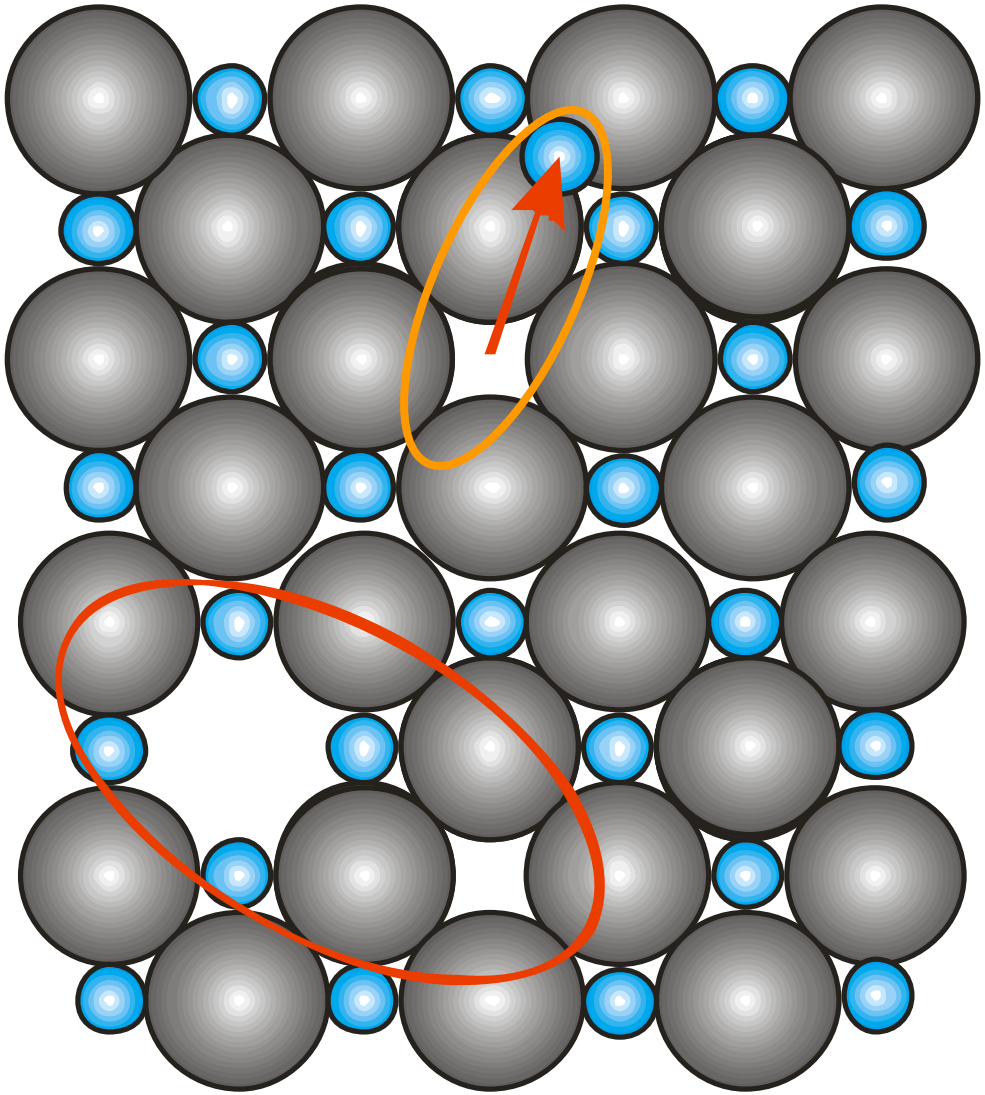
fig. 17



Frenkel defect

Frenkel defect – Point defect where an atom / ion has been displaced into an interstital site. eg In AgCl some Ag^+ ions occupy tetrahedral sites (fig. 16) which are normally unoccupied. Stoichiometry is unchanged.

https://www.unf.edu/~michael.lufaso/chem4627/ch5_solid_state.pdf



Frenkel defect

Cation vacancy
+
cation interstitial

Schottky defect

Cation vacancy
+
anion vacancy

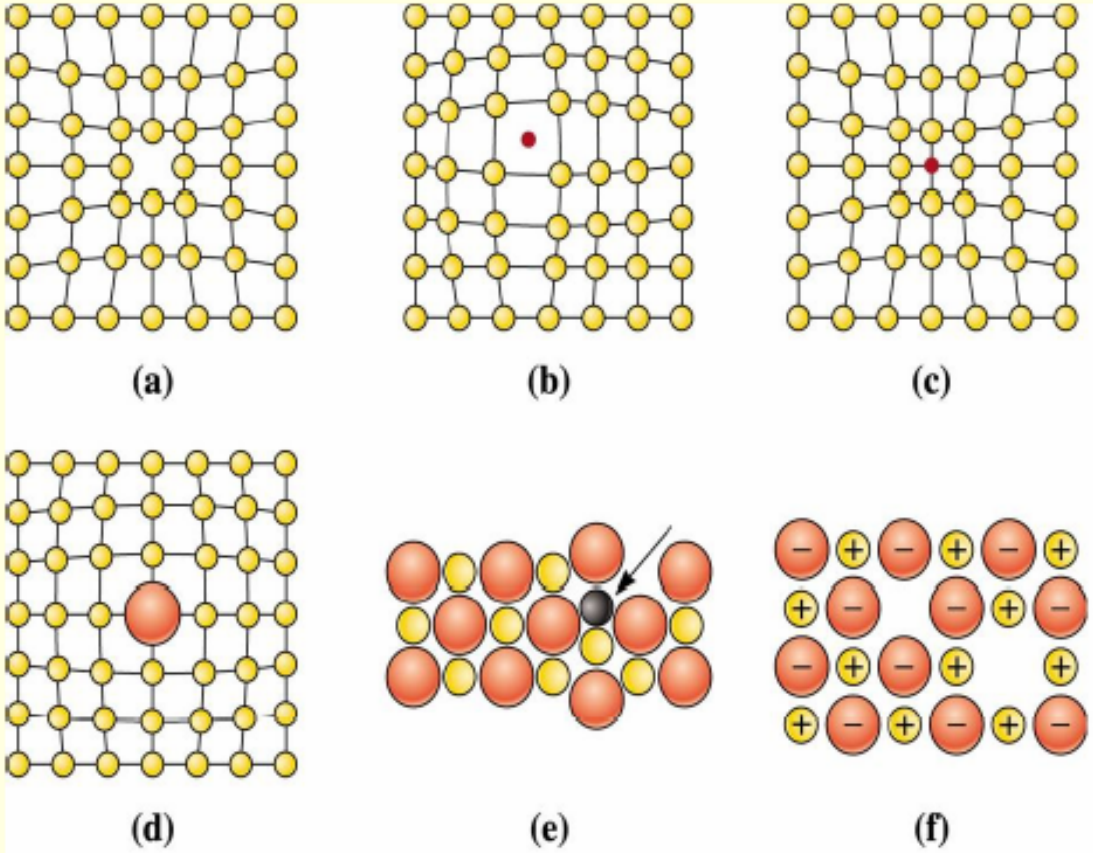


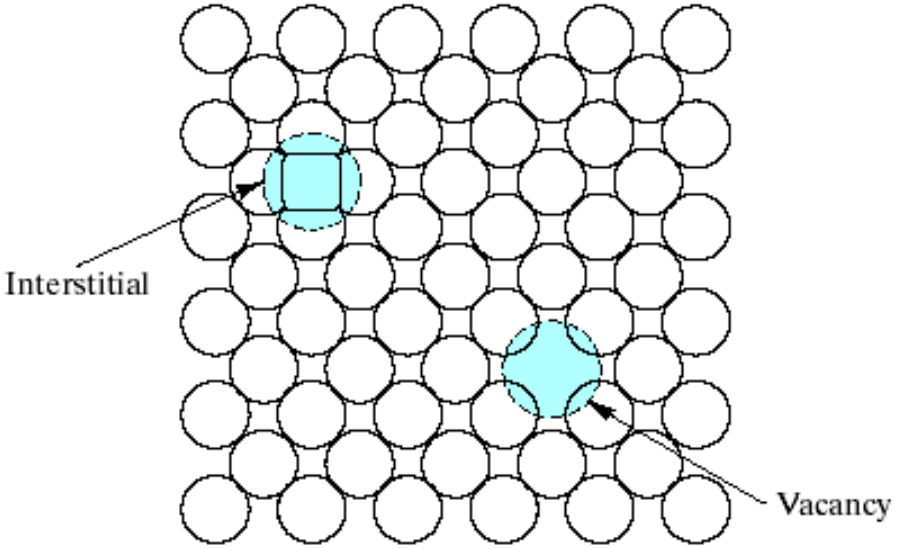
Figure 4-1 Point defects: (a) vacancy, (b) interstitial atom, (c) small substitutional atom, (d) large substitutional atom, (e) Frenkel defect, and (f) Schottky defect. All of these defects disrupt the perfect arrangement of the surrounding atoms.

- **Schottky defect**
  - A pair of oppositely charged ion vacancies

- **Frenkel defect**
  - A vacancy-interstitialcy combination

Vacancies

- "Origin" of vacancies
  - In elemental and metallic solids
  - In ionic solids



- **Vacancy**
  - Unoccupied atom site
- **Interstitial**
  - An atomic occupying an interstitial site

Hume-Rothery rules for complete solid solution

- The size difference between the solute and solvent must be no greater than ~15 %.

$$Mismatch = \left(\frac{r_{solute} - r_{solvent}}{r_{solvent}} \right) \times 100 \leq 15\%$$

- The electronegativity of the two atomic species must be comparable.
- The valence of the two species must be similar.
- The crystal structures of the two species must be the same.

Electronegativity, symbol **χ**, is a chemical property that describes the ability of an atom (or, more rarely, a functional group) to attract electrons (or electron density) towards itself in a covalent bond.

- A metal with a lower valency is more likely to dissolve in one which has a higher valency, than *vice versa*.

- A *quasicrystal* has long-range order but lacks translational periodicity in three dimensions.

Impurities Impurities - atoms which are different from the host.

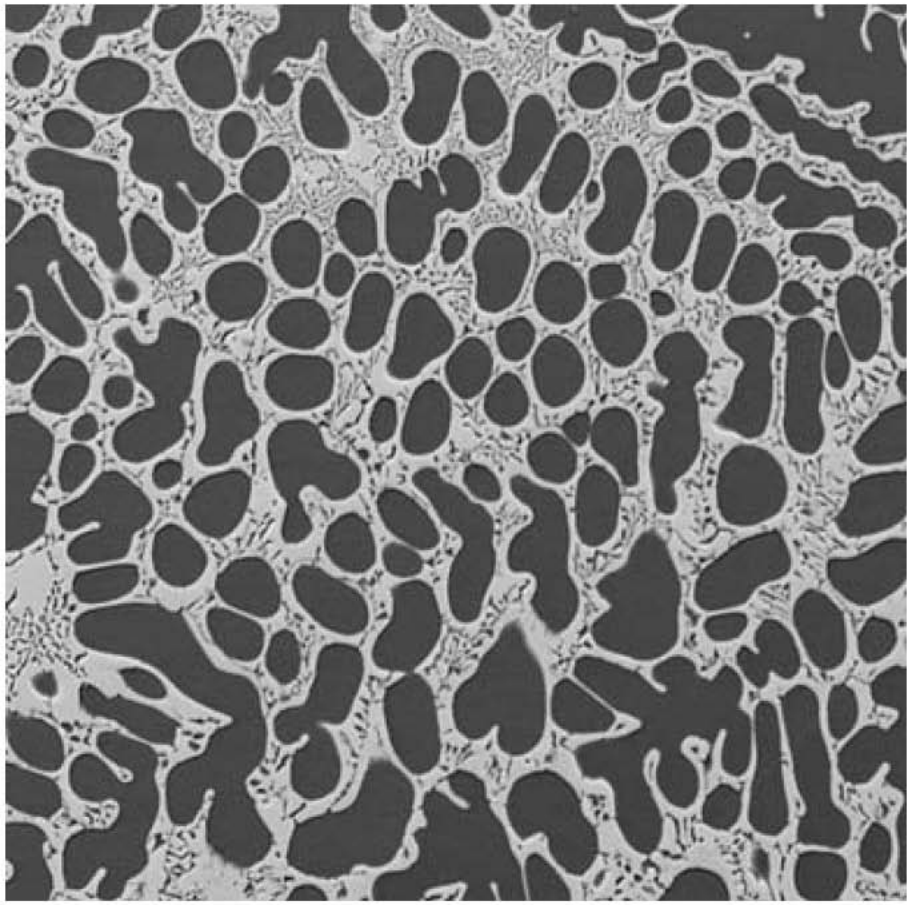
•All real solids are impure. Very pure metals 99.9999% - one impurity per 10^6 atoms .

•May be intentional or unintentional :

Examples: carbon added in small amounts to iron makes steel, which is stronger than pure iron. Boron added to silicon change its electrical properties.

•Alloys - deliberate mixtures of metals Example: sterling silver is 92.5% silver – 7.5% copper alloy. Stronger than pure silver.

http://web.utk.edu/~prack/mse201/Chapter%204%20Defects.pdf



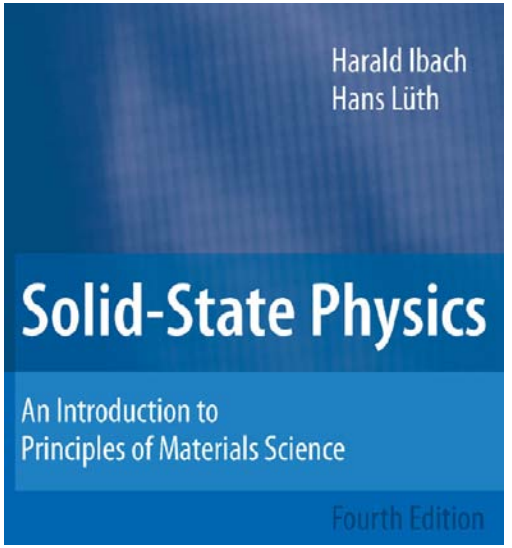
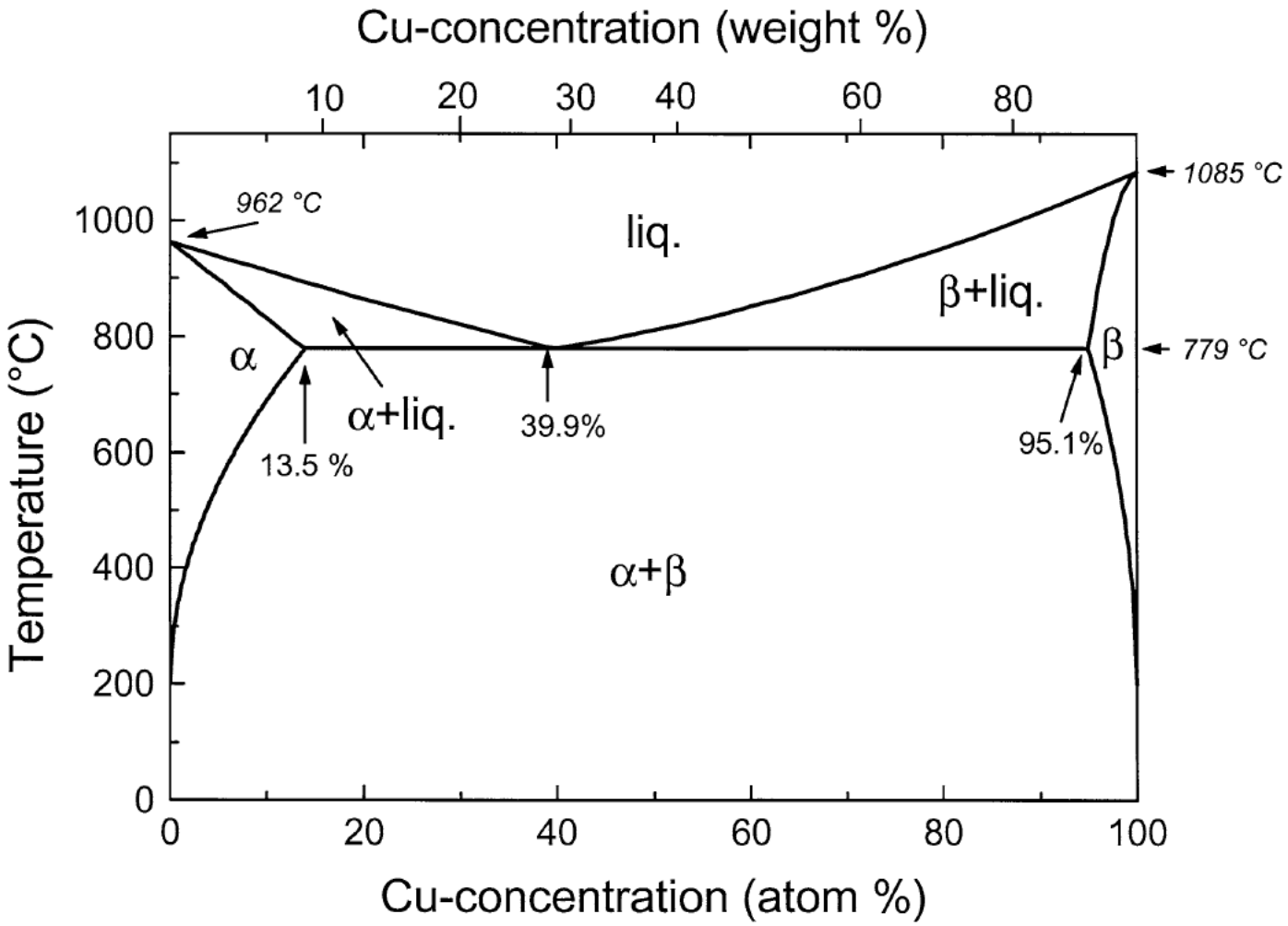


Fig. 2.13. Scanning electron microscope image of a polished specimen of an Ag/Cu alloy with 30% Ag- and 70% Cu-atoms. The dark and light areas consist of fcc-phases with about 95% Cu-atoms and about 86% Ag-atoms, respectively



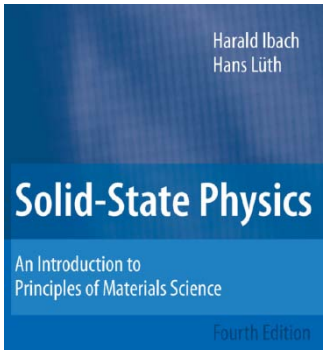
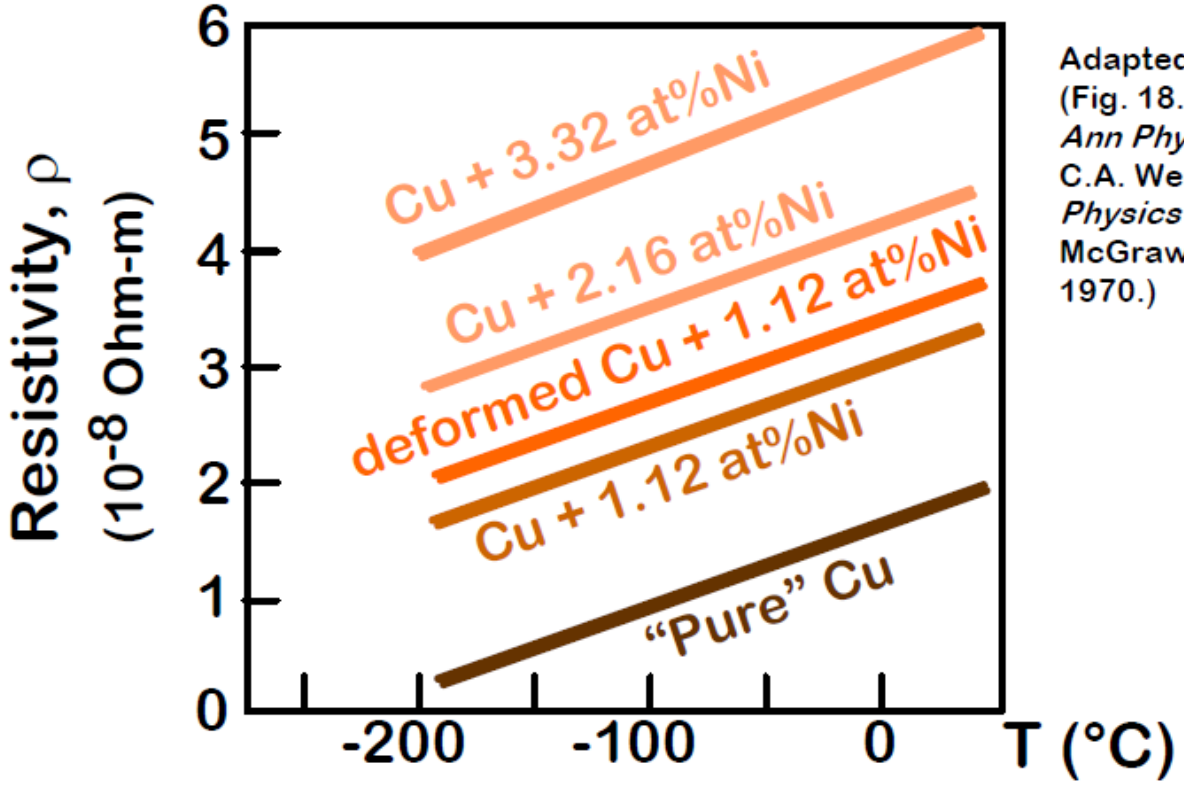


Fig. 2.15. Phase diagram for the binary alloy Ag/Cu. The system is not continuously miscible in the solid phase. Rather the alloy has a wide miscibility gap in which a Ag-rich fcc-phase (α-phase) co-exists with a Cu-rich fcc-phase (β-phase) (see Fig. 2.13)

Substitutional defects

- Electrical Resistivity of Copper:



Adapted from Fig. 18.8, *Callister 6e.* (Fig. 18.8 adapted from: J.O. Linde, *Ann Physik* **5**, 219 (1932); and C.A. Wert and R.M. Thomson, *Physics of Solids*, 2nd edition, McGraw-Hill Company, New York, 1970.)

- Adding "impurity" atoms to Cu increases resistivity.
- Deforming Cu increases resistivity.

Substitutions in Ionic Solids

- Rules for substitution
  - Similarity of sites
  - Charge balance
- Effect on ionic conductivity

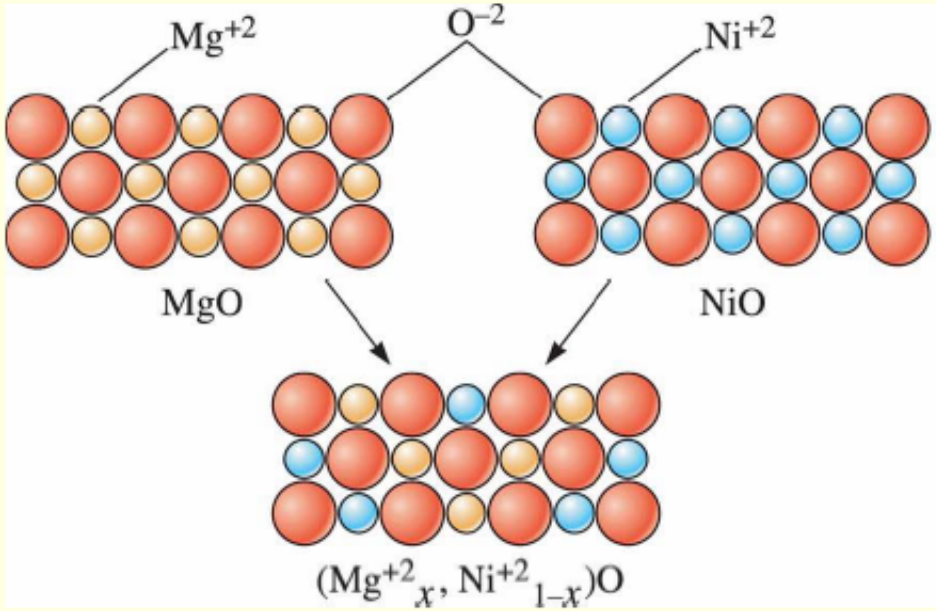
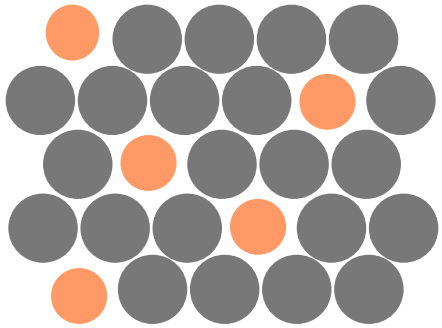


Figure 10-6
MgO and NiO have similar crystal structures, ionic radii, and valences; thus the two ceramic materials can form solid solutions.

Point Defects in Alloys

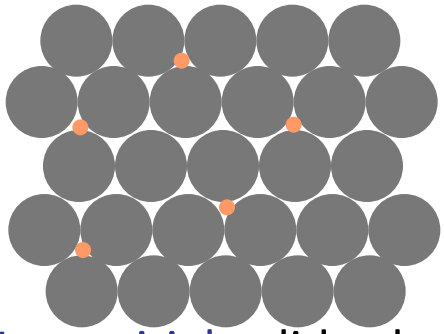
Two outcomes if impurity (B) added to host (A):

- Solid solution of B in A (i.e., random dist. of point defects)



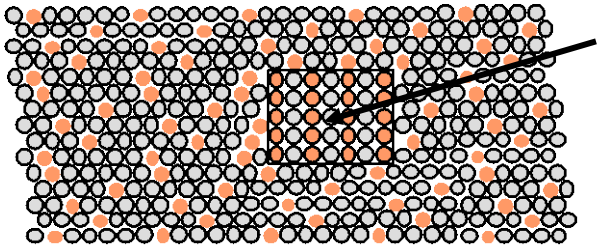
Substitutional solid soln.
(e.g., Cu in Ni)

OR



Interstitial solid soln.
(e.g., C in Fe)

- Solid solution of B in A plus particles of a **new phase** (usually for a larger amount of B)



Second phase particle
--different composition
--often different structure.

Linear Defects or

Dislocations

- Origin of dislocations
- Types of dislocations

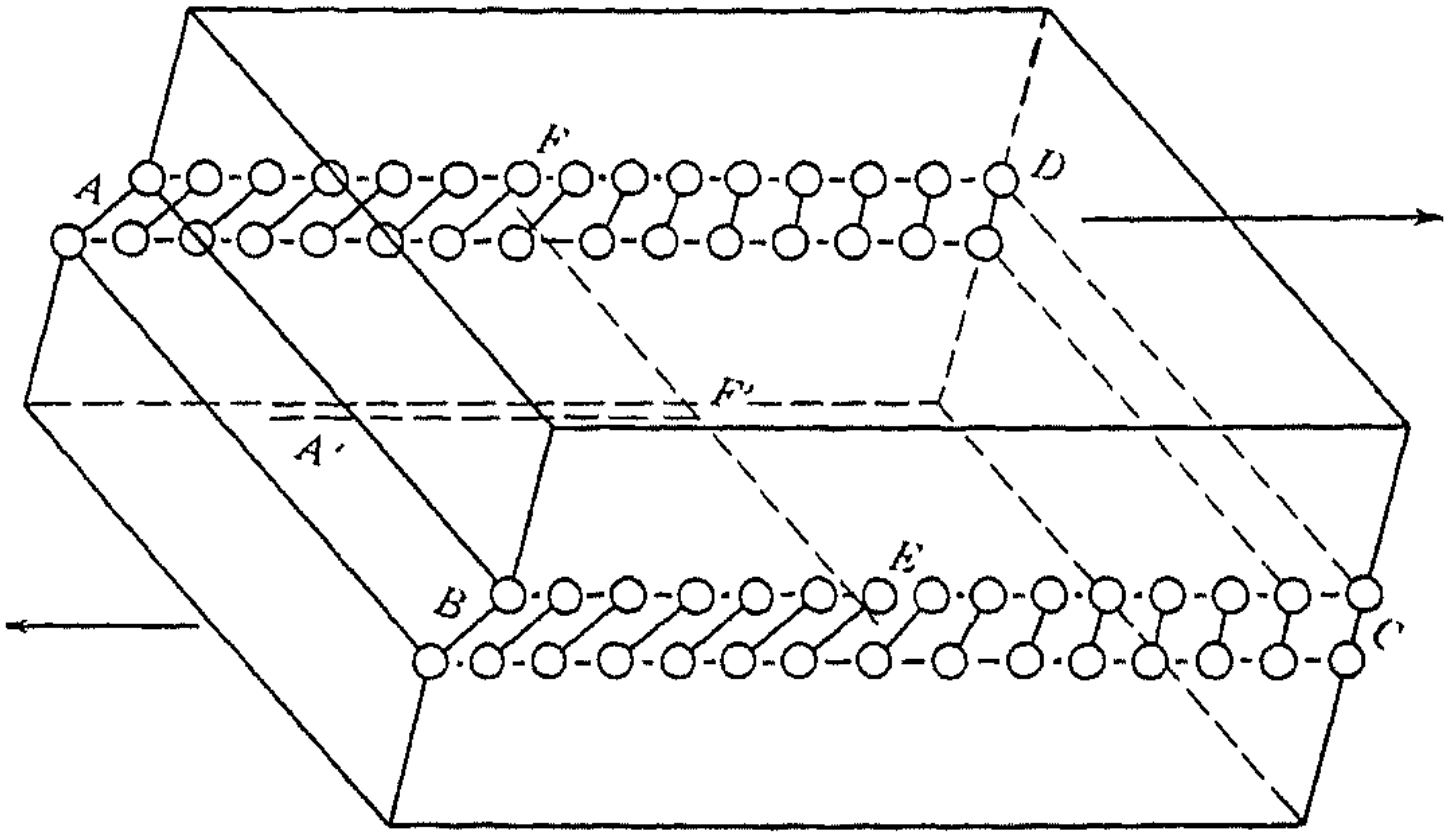
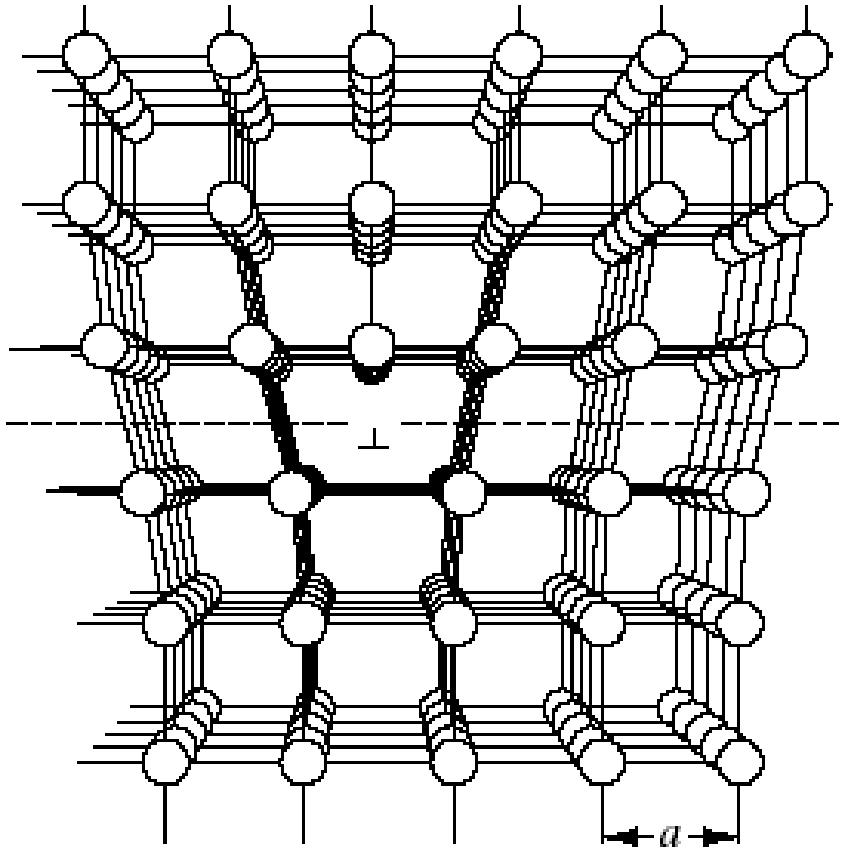


Fig. 16.1. An edge dislocation, showing the glide plane $ABCD$, the slipped region $ABEF$ in which the atoms have been displaced by more than half a lattice constant, and the unslipped region $FECD$ with displacement less than half a lattice constant. The dislocation line is EF and the slip direction is $A'F'$. (After Cottrell, *Progress in metal physics*, No. 1, Butterworths Scientific Publications, London, 1949.)

- Linear defects or dislocations : Associated with mechanical deformation



⊥

Represents the edge of an extra half plane of atoms

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Edge Dislocation

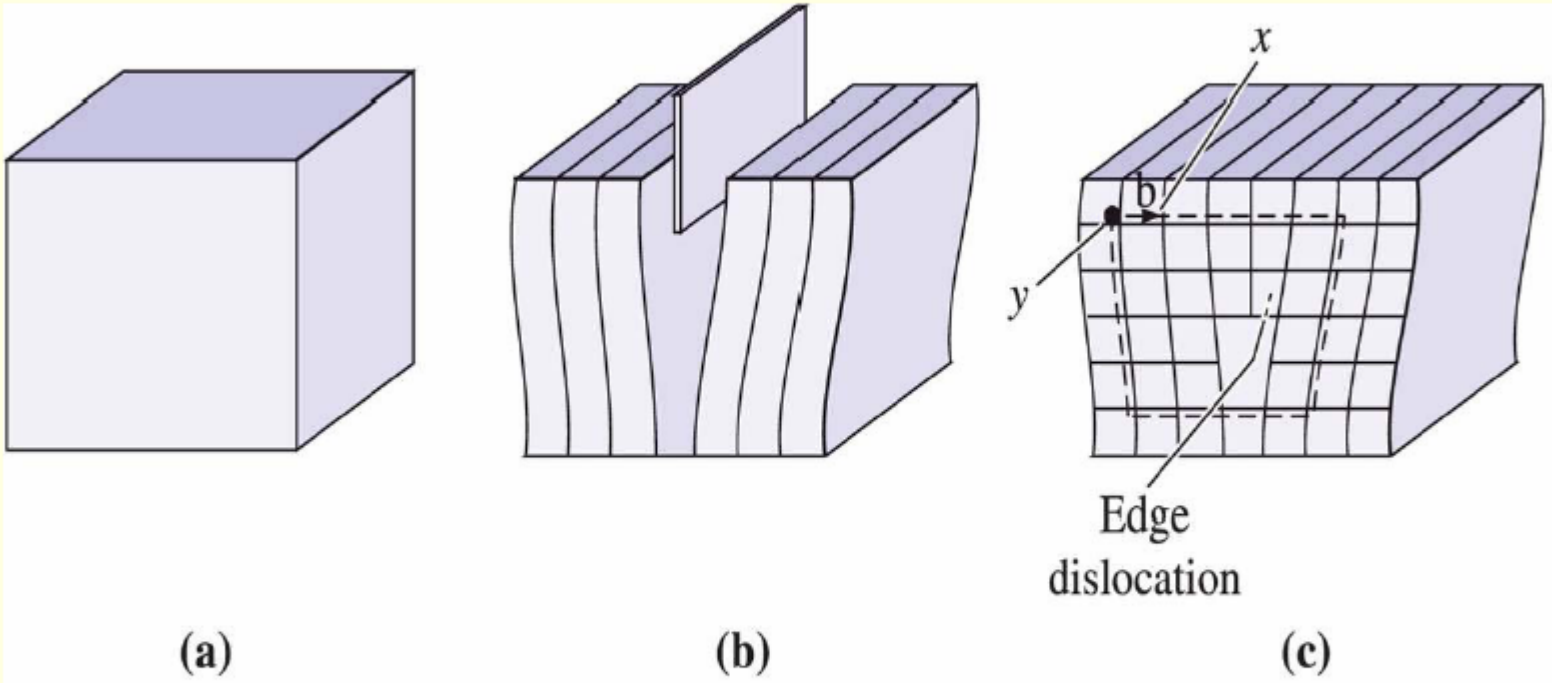
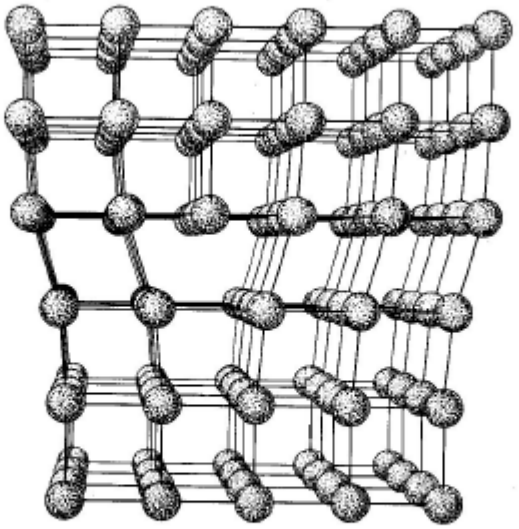


Figure 4-5 The perfect crystal in (a) is cut and an extra plane of atoms is inserted (b). The bottom edge of the extra plane is an edge dislocation (c). A Burgers vector **b** is required to close a loop of equal atom spacings around the edge dislocation. *(Adapted from J.D. Verhoeven, Fundamentals of Physical Metallurgy, Wiley, 1975.)*

Dislocations are *line defects*. Simplest to visualize is an *edge dislocation* – think of an extra half-plane of atoms.

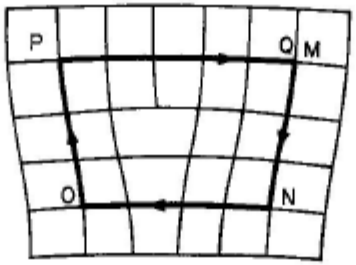


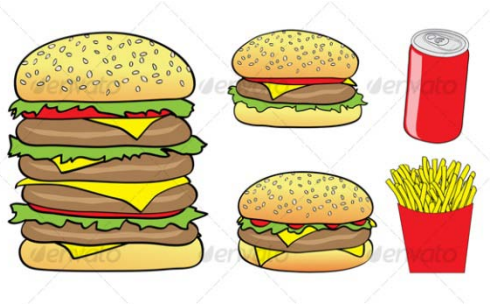
Affects deformation properties – to slide upper block over lower now only requires a *line* of bonds to break at a time, not a whole *plane* – process of *slip*. Explains low yield strength of solids.

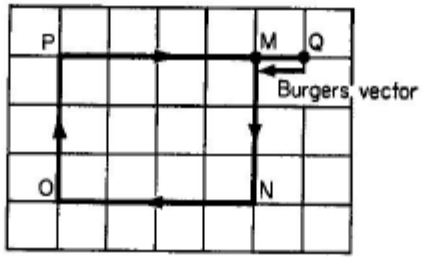
http://academic.uprm.edu/pcaceres/Courses/MatEng/MSE4-1.pdf

http://bibing.us.es/proyectos/abreproy/80016/fichero/chapter+2.pdf

Dislocations are characterised by their *Burgers vectors* – the mismatch in position between going round a path in the perfect crystal or round the dislocation.







Edge: b perpendicular to line of dislocation. Screw: b parallel to line of dislocation.

http://academic.uprm.edu/pcaceres/Courses/MatEng/MSE4-1.pdf

Screw Dislocation

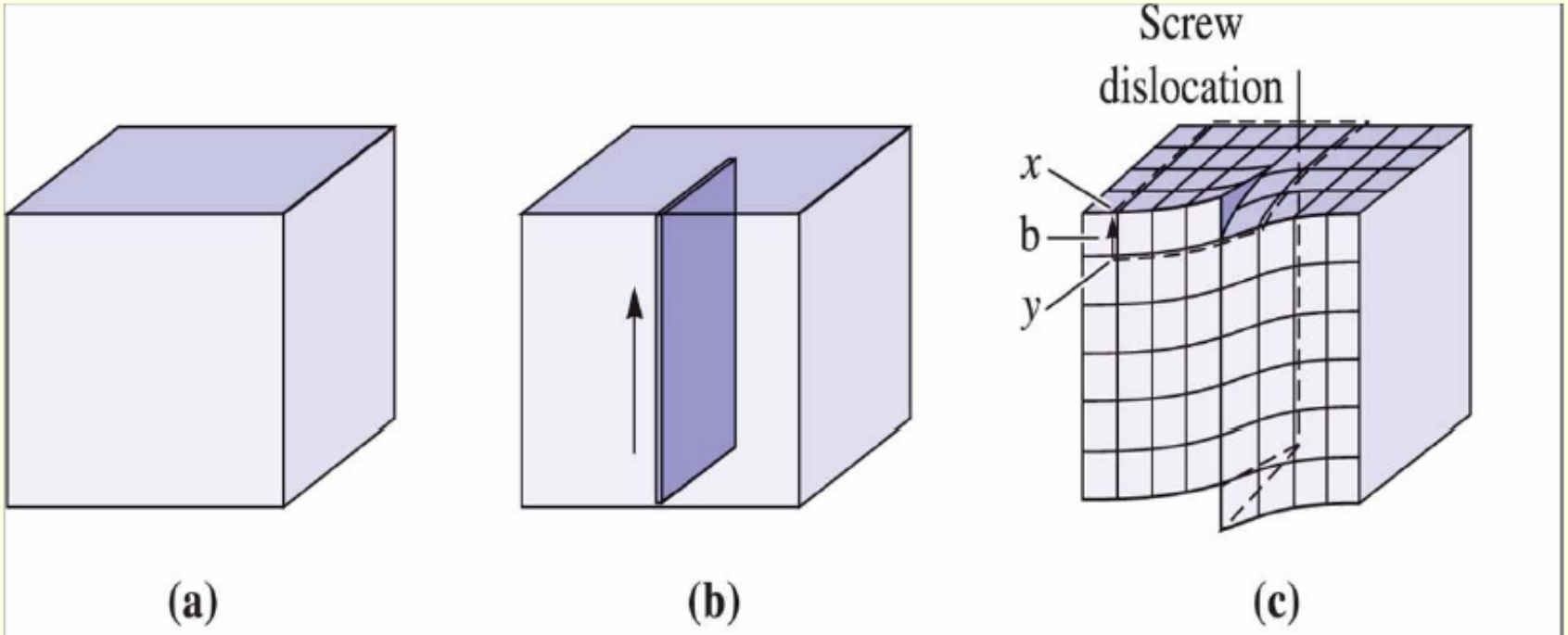
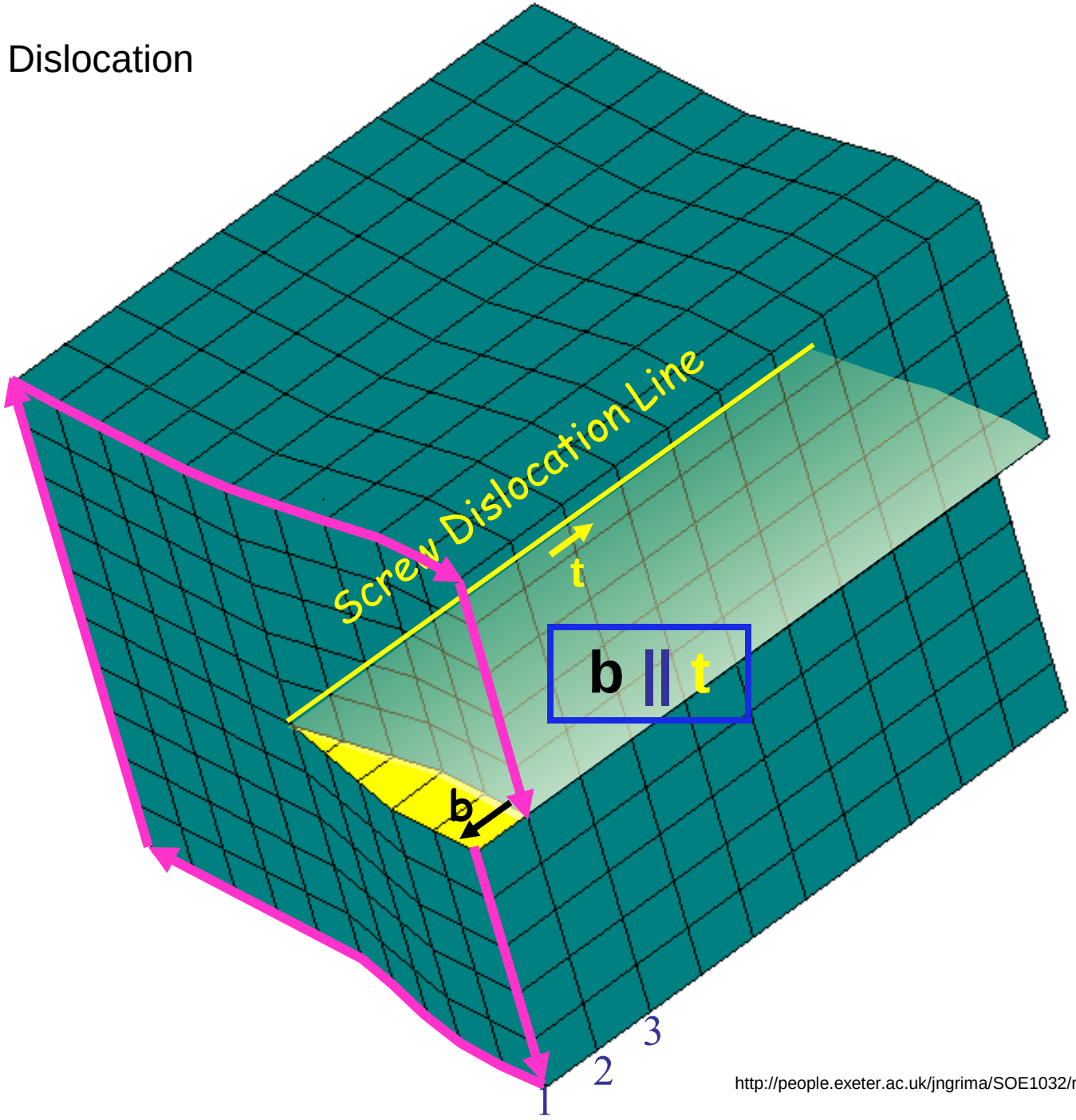


Figure 4-4 The perfect crystal (a) is cut and sheared one atom spacing, (b) and (c). The line along which shearing occurs is a screw dislocation. A Burgers vector **b** is required to close a loop of equal atom spacings around the screw dislocation.

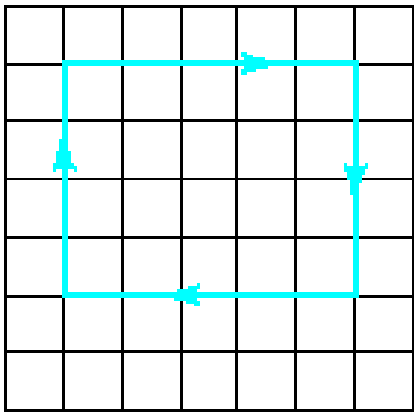
Screw Dislocation



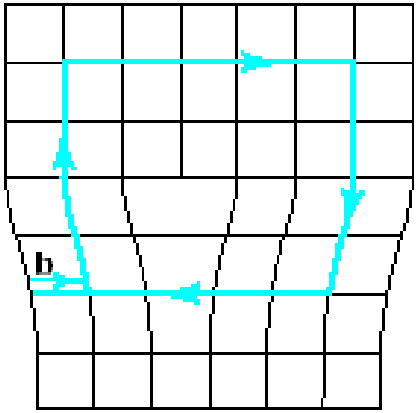
http://people.exeter.ac.uk/jngrima/SOE1032/rmh_q3/dislocations.html

Screw dislocation

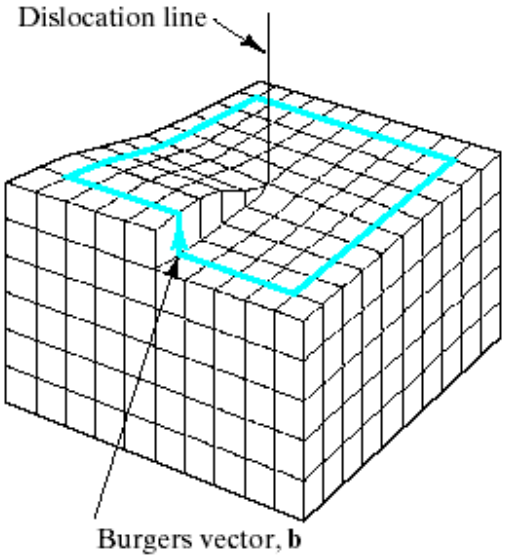
Mixed dislocation

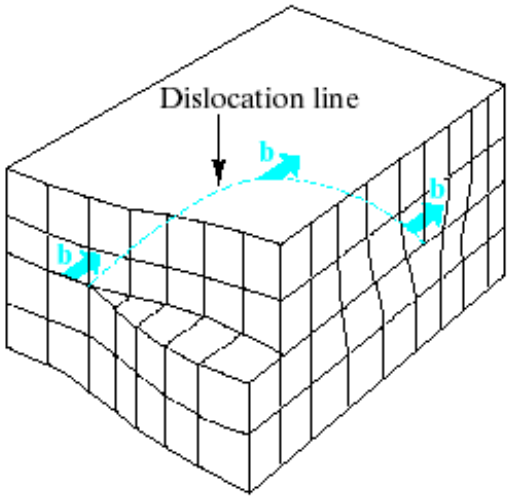


(a)



(b)

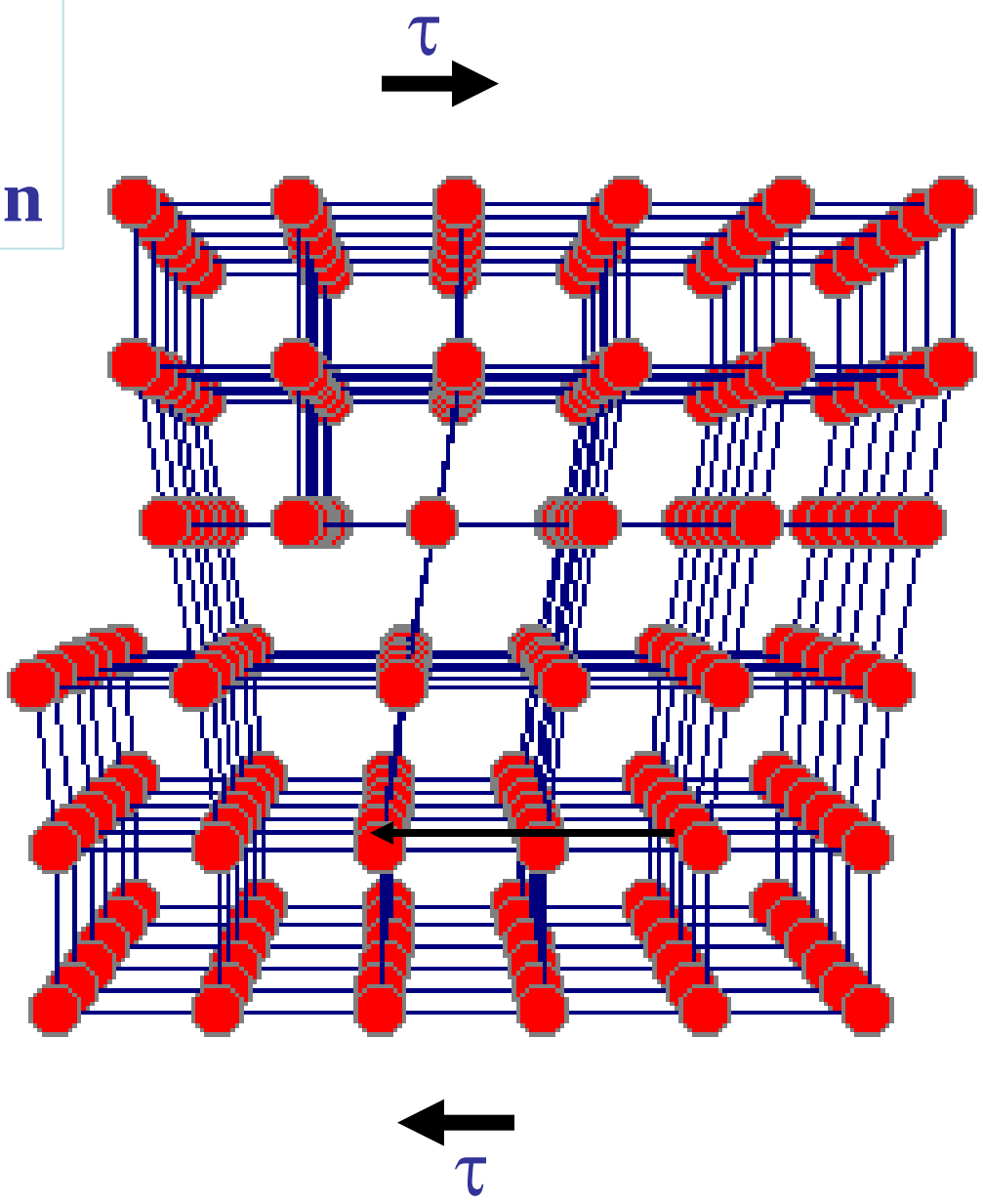




- Burgers vector, b is simply the displacement vector necessary to close a stepwise loop around the defect.
  - For the edge dislocation b is perpendicular to the dislocation line.
  - For the screw dislocation b is parallel to the dislocation line.
  - Mixed dislocation has both edge and screw character.

http://academic.uprm.edu/pcaceres/Courses/MatEng/MSE4-1.pdf

Glide of an Edge Dislocation



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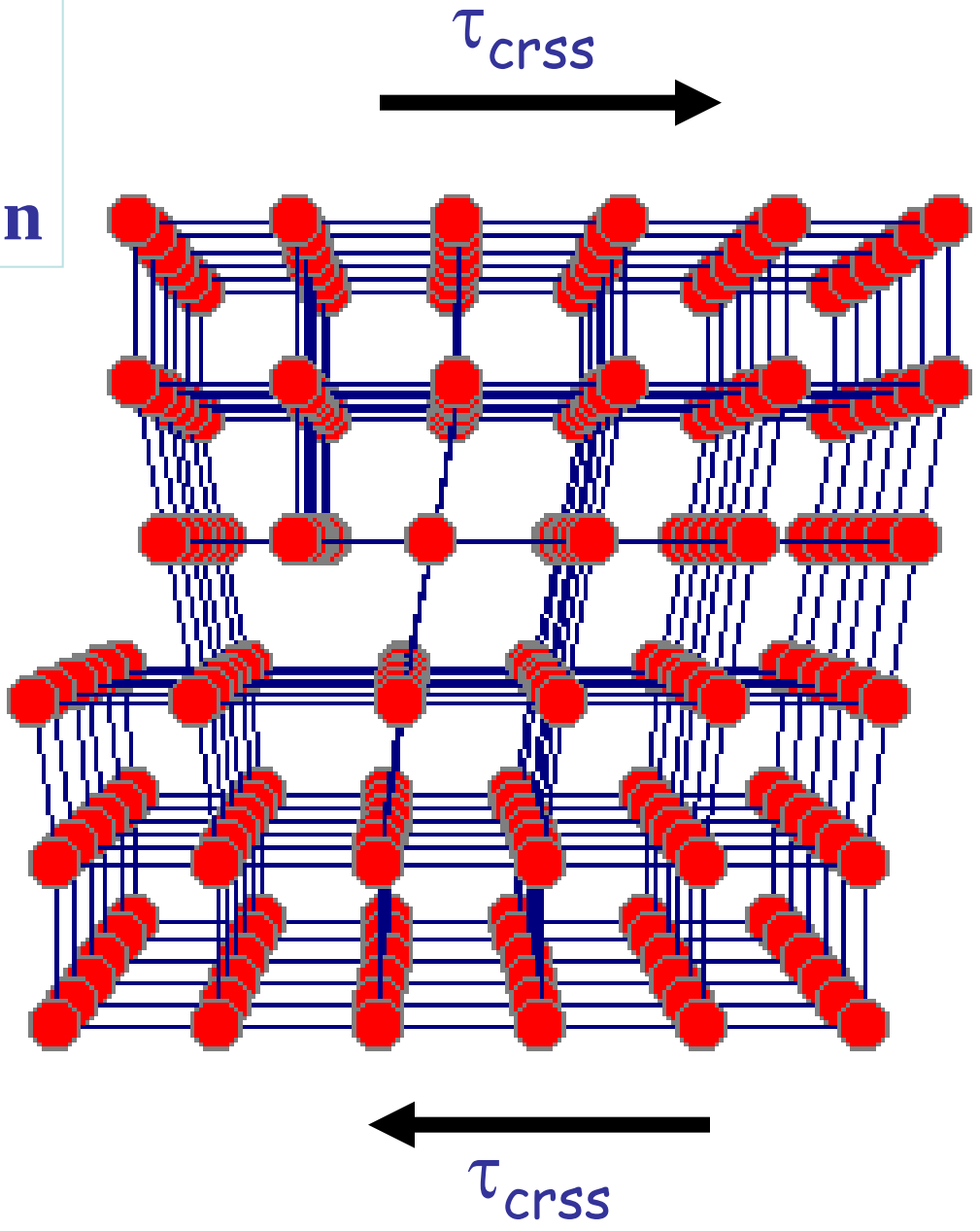
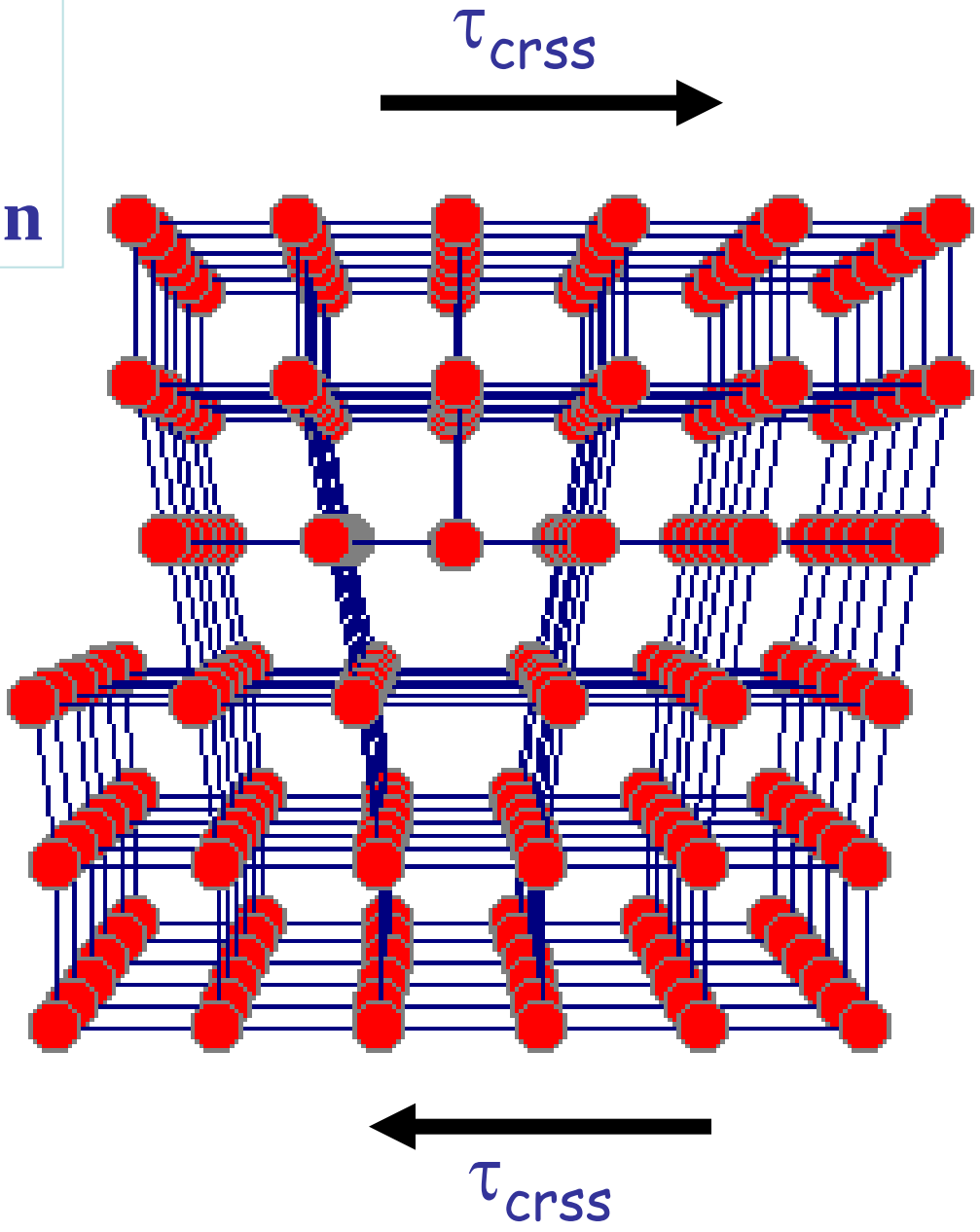
Glide of an Edge Dislocation



τ_{crss} is critical resolved shear stress on the slip plane in the direction of b.

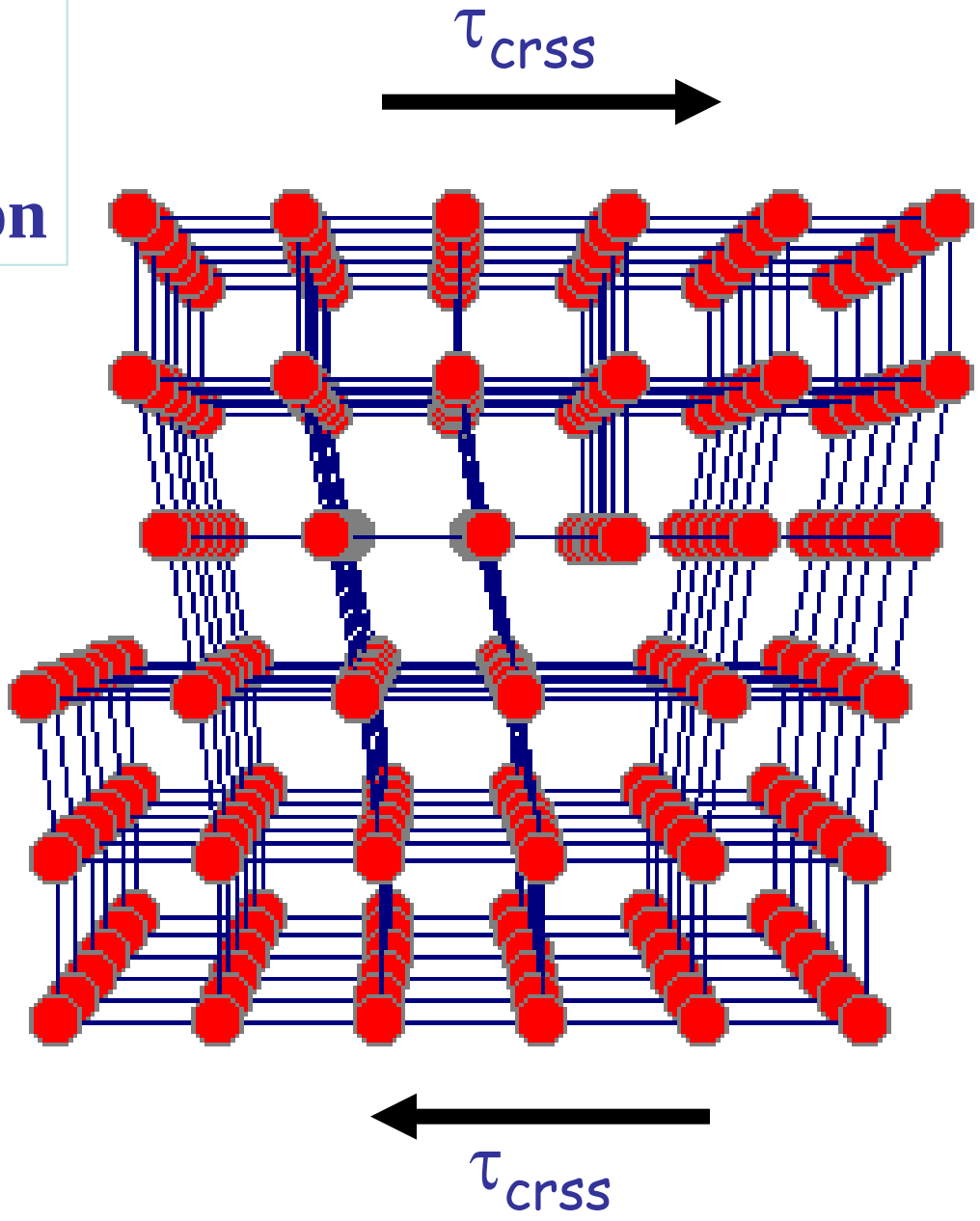
Glide of an Edge Dislocation



τ_{crss} is critical resolved shear stress on the slip plane in the direction of b.

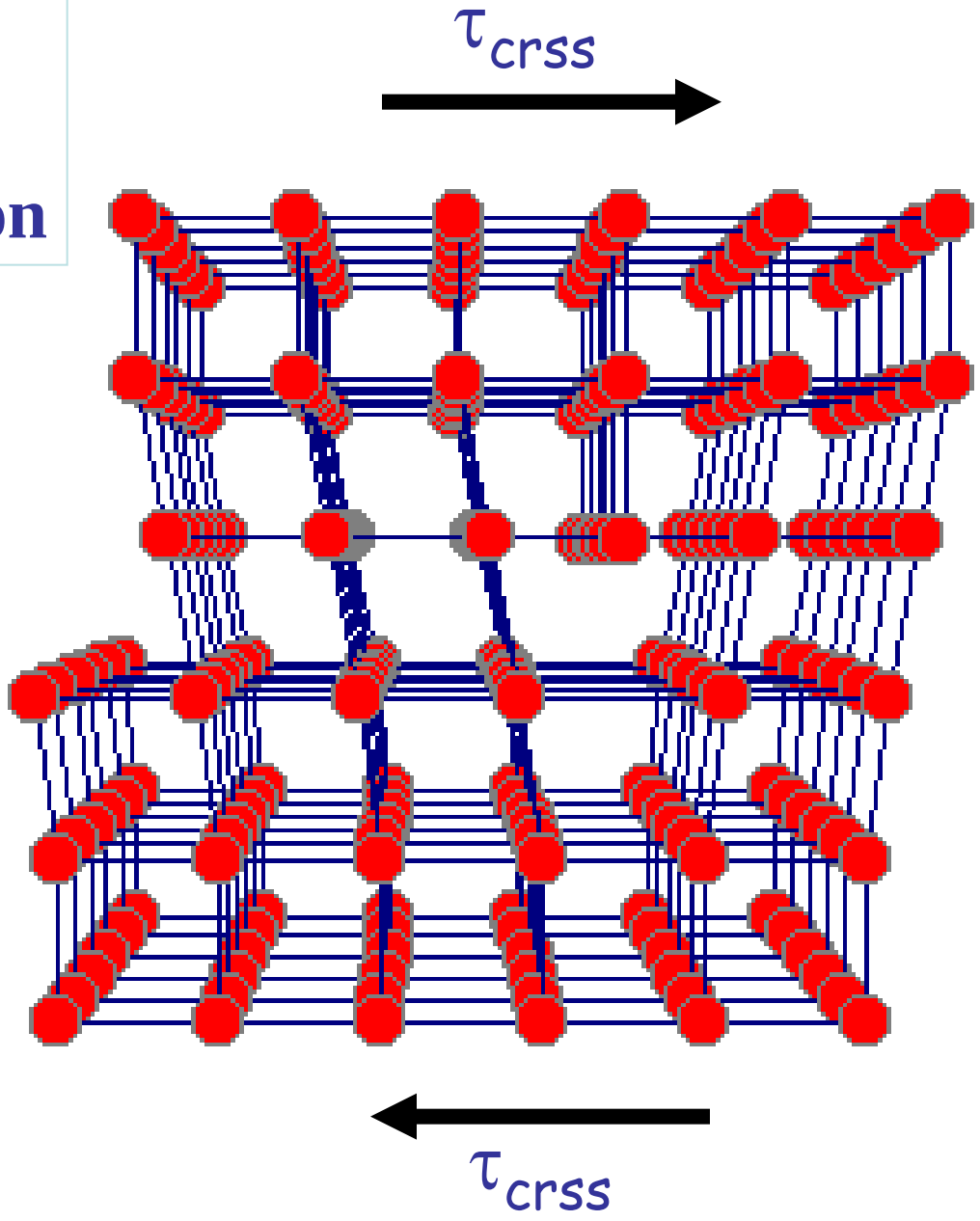
http://www.slideshare.net/MayurBagale/imperfections-innew2?next_slideshow=3

Glide of an Edge Dislocation



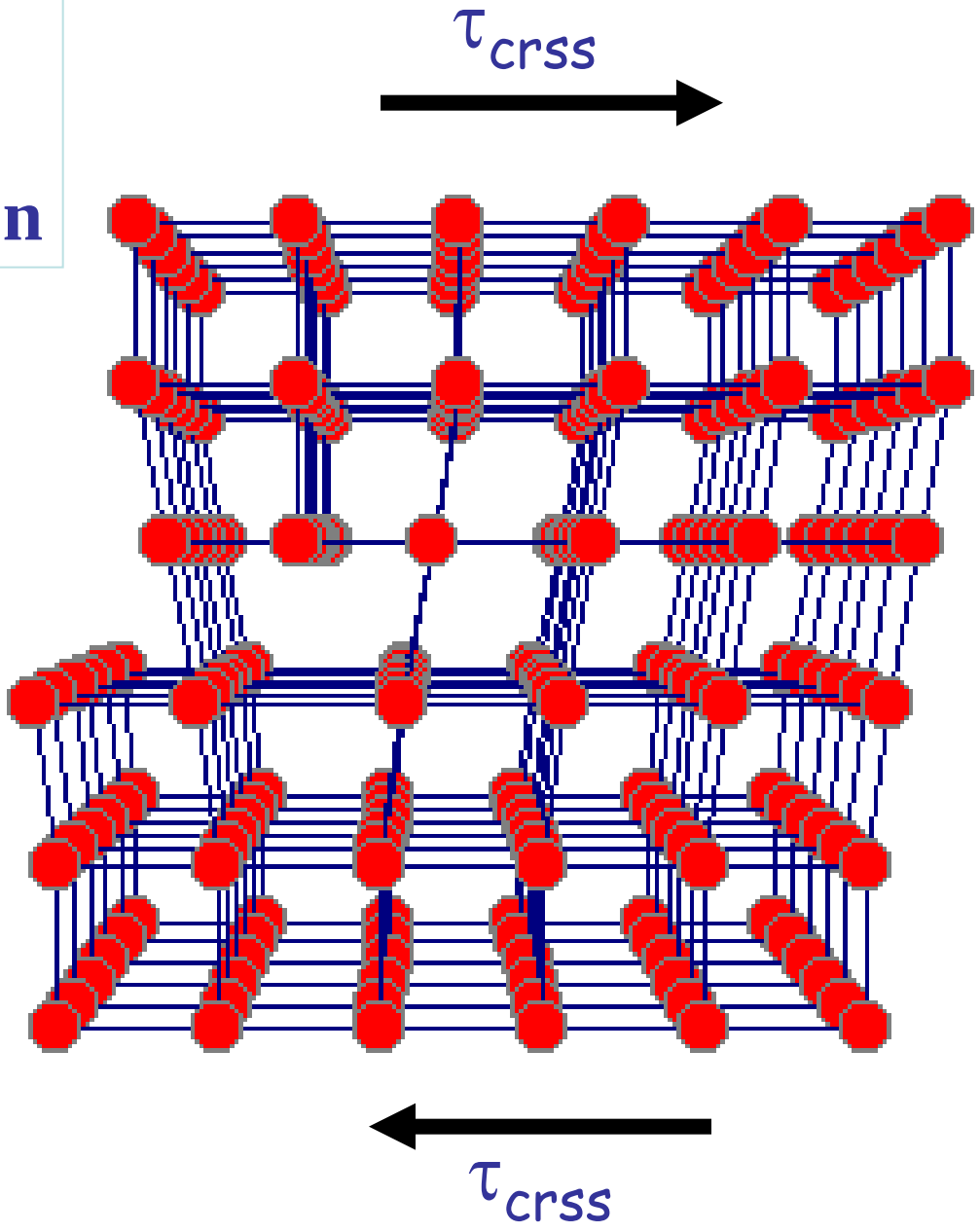
τ_{crss} is critical resolved shear stress on the slip plane in the direction of b.

Glide of an Edge Dislocation



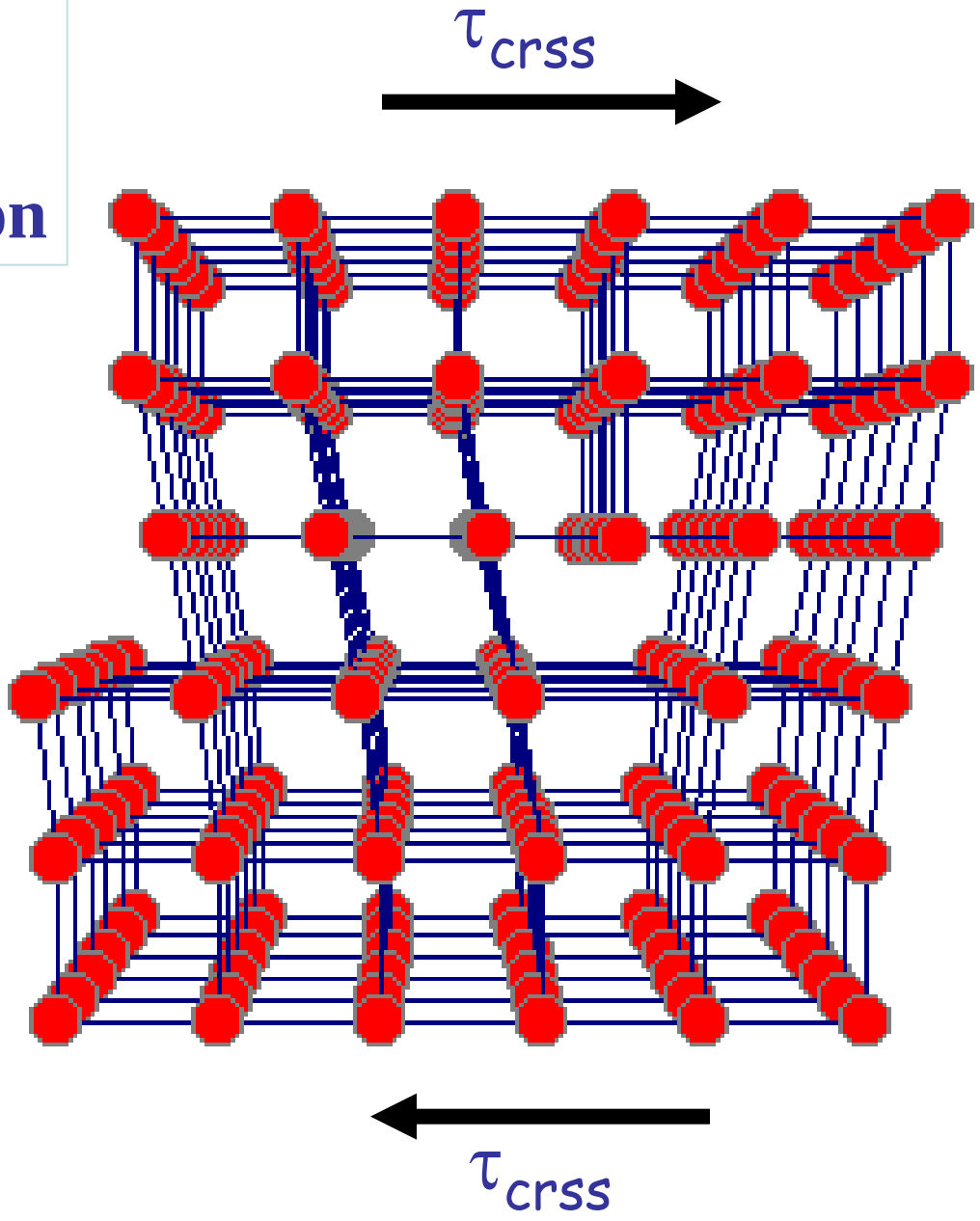
τ_{crss} is critical resolved shear stress on the slip plane in the direction of b.

Glide of an Edge Dislocation



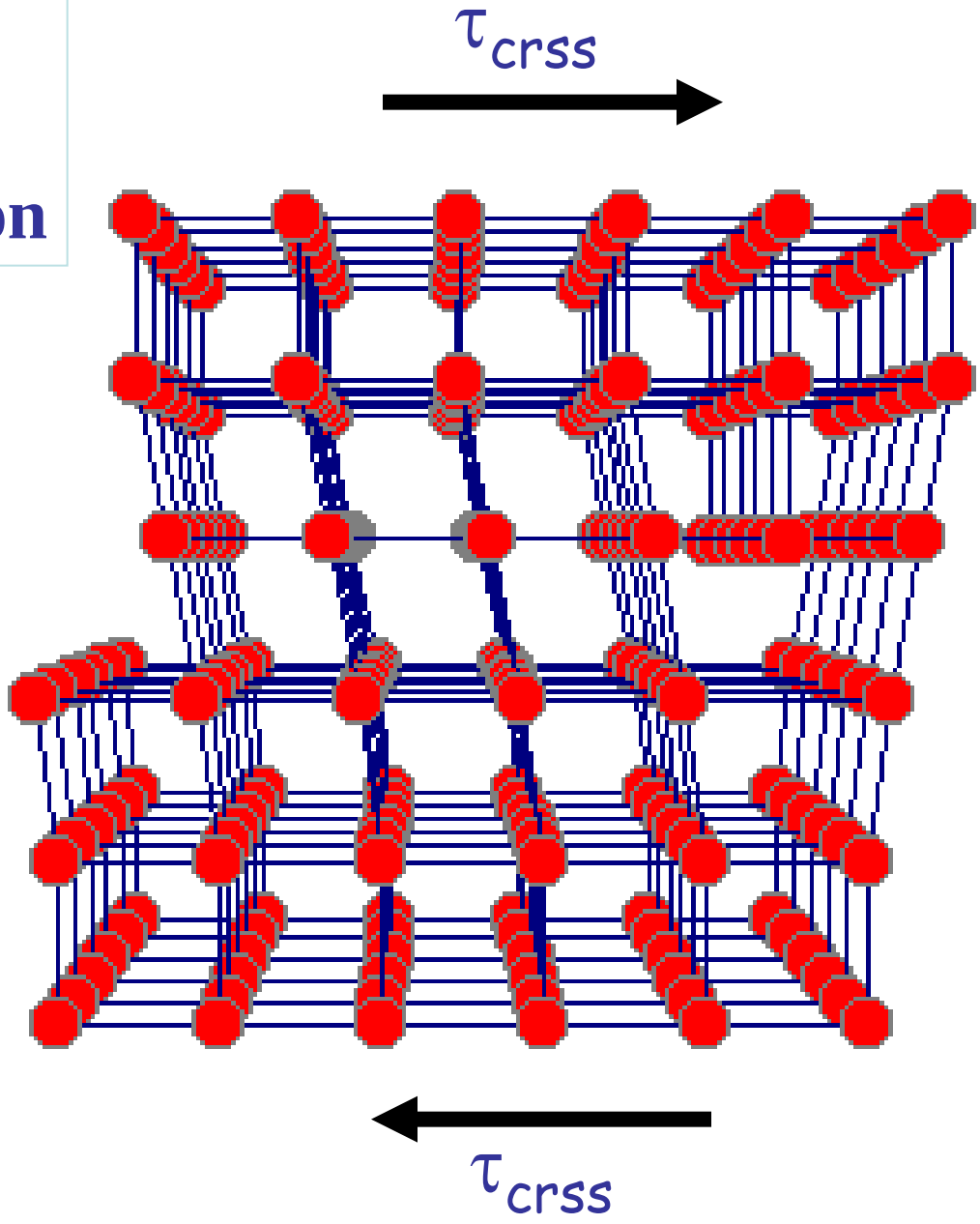
τ_{crss} is critical resolved shear stress on the slip plane in the direction of b.

Glide of an Edge Dislocation



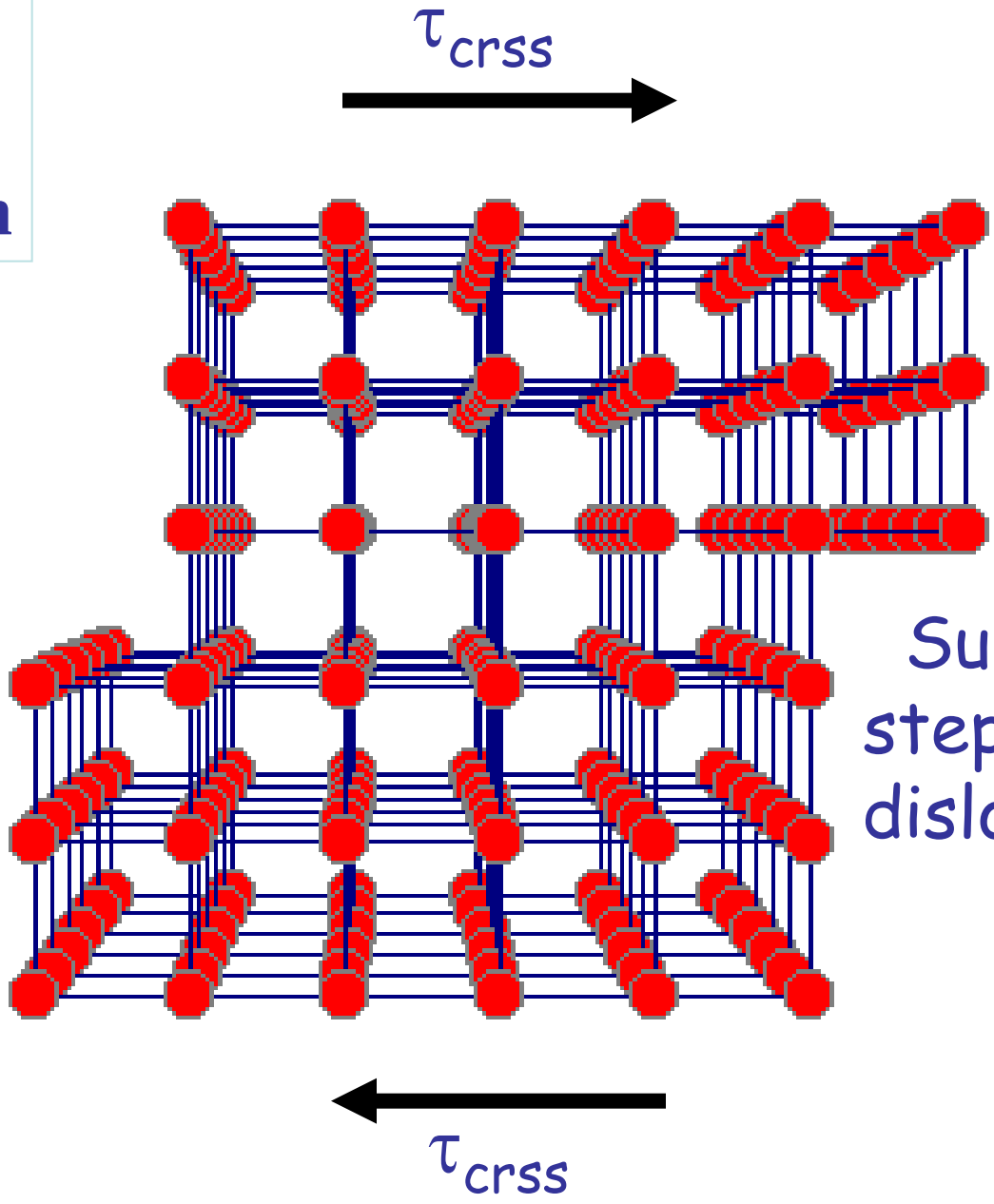
τ_{crss} is critical resolved shear stress on the slip plane in the direction of b.

Glide of an Edge Dislocation



http://www.slideshare.net/MayurBagale/imperfections-innew2?next_slideshow=3

Glide of an Edge Dislocation



A surface step of b is created if a dislocation sweeps over the entire slip plane

Surface step, not a dislocation

http://www.slideshare.net/MayurBagale/imperfections-innew2?next_slideshow=3

A dislocation line cannot end abruptly inside a crystal

It can end on

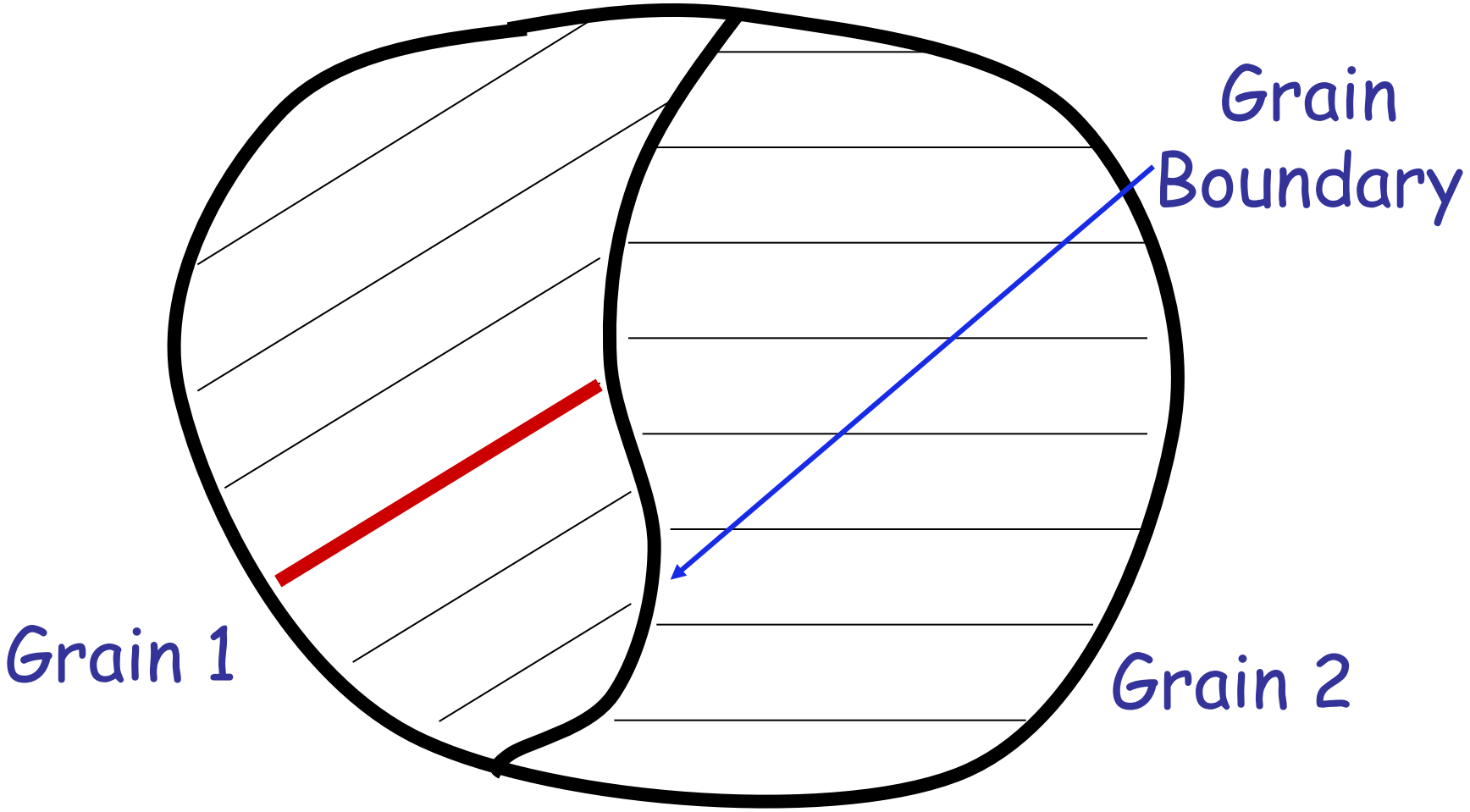
Free surfaces

Grain boundaries

On other dislocations at a point called a node

On itself forming a loop

Dislocation can end on a grain boundary



Transmission electron micrograph of dislocations

https://en.wikipedia.org/wiki/Dislocation#/media/File:TEM_micrograph_dislocations_precipitate_stainless_steel_1.jpg

A growth spiral on a silicon carbide crystal, originating from the point of emergence of a screw dislocation (courtesy Prof. S. Amelinckx).

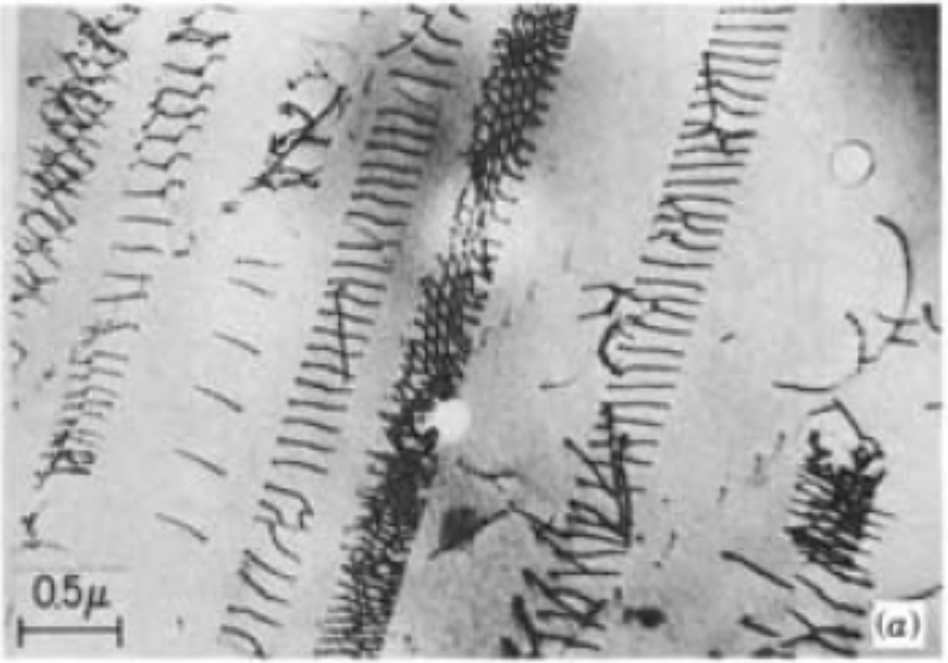
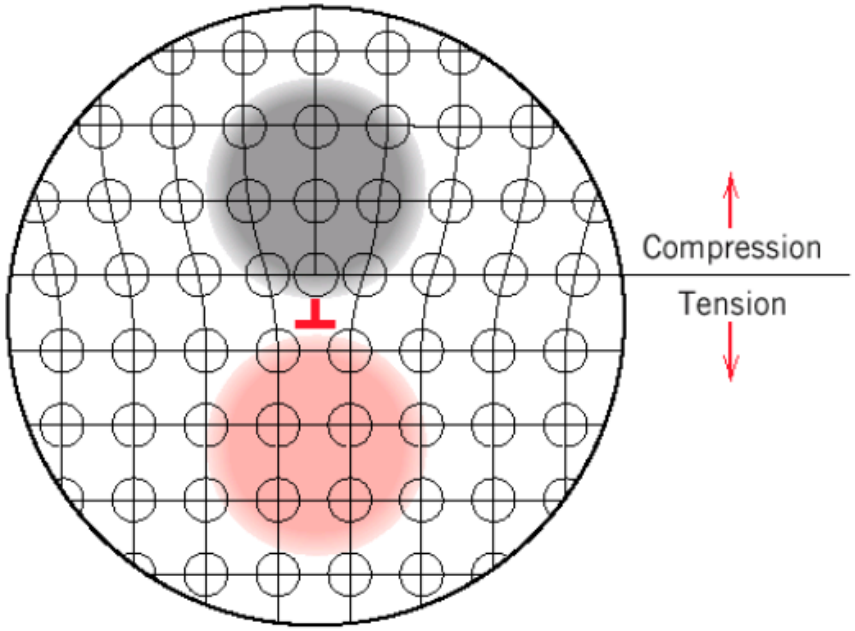


FIGURE 2.13 Observation of individual dislocations in thin foil. (*a*) Planar arrays of dislocations in 18Cr–8Ni stainless steels (from Michalak,[10] *Metals Handbook*, Vol. 8, copyright American Society for Metals, Metals Park, OH, 1973; used with permission); (*b*) diagram showing position of dislocations on the guide plane in the foil (after Hull[11]).

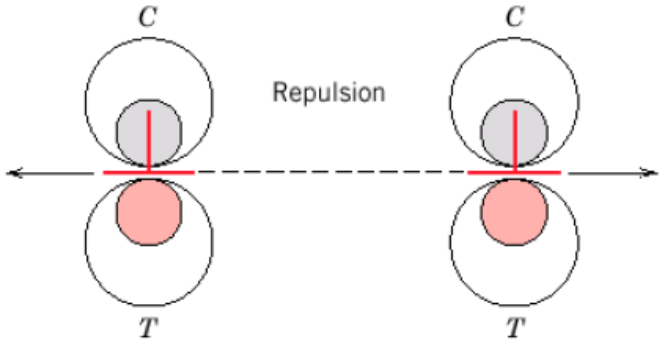


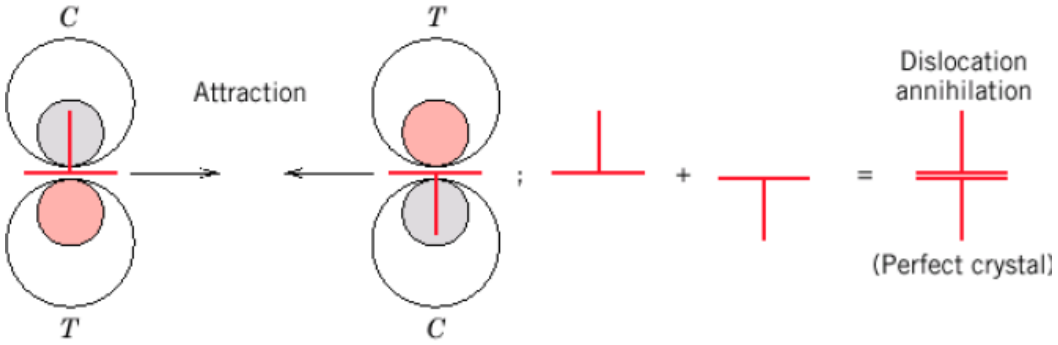
Dislocations have strain fields arising from distortions at their cores - strain drops radially with distance from dislocation core

Edge dislocations introduce compressive, tensile, and shear lattice strains, screw dislocations introduce shear strain only.

http://web.utk.edu/~prack/mse201/Chapter%207%20Dislocations%20.pdf

Interactions between Dislocations





The strain fields around dislocations cause them to interact (exert force on each other). When they are in the same plane, they repel if they have the same sign (direction of the Burgers vector) and attract/annihilate if they have opposite signs.

http://web.utk.edu/~prack/mse201/Chapter%207%20Dislocations%20.pdf

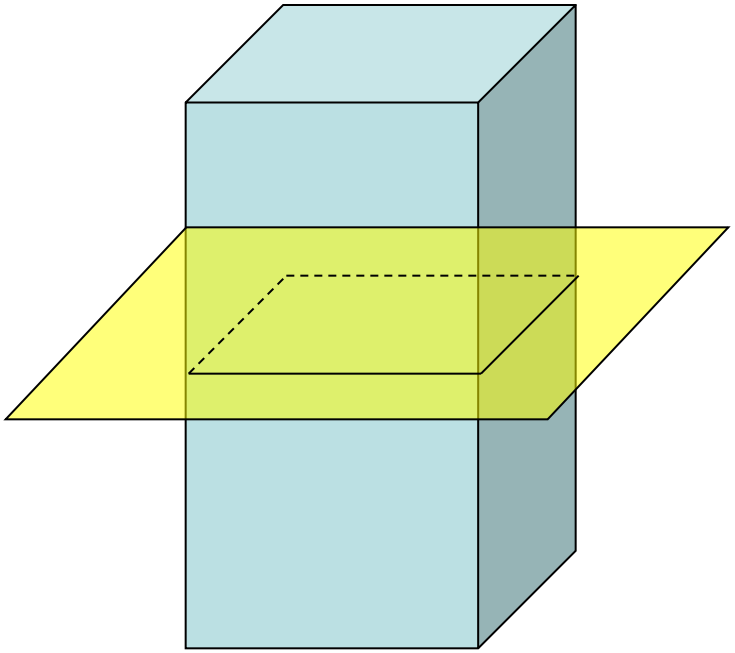
- ✓ A dislocation is a lattice line defect.
- ✓ The *line* or *dislocation* defines the boundary between *slipped* and *unslipped* portions of the crystal.
- ✓ Dislocations can terminate at:
  - o free surface
  - o boundaries (e.g., grain boundary, interface, etc.).
  - o Another dislocation
- ✓ Dislocations can never terminate within the crystal.
- ✓ Consequently, dislocations must either form:

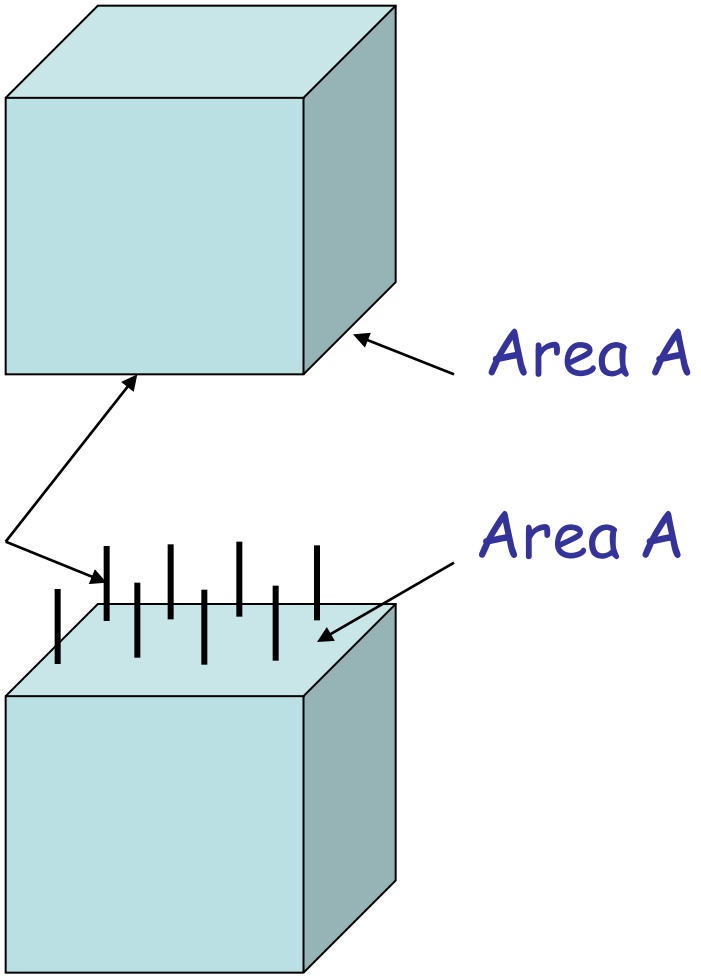
Closed loops

Or:
networks with *branches* that *terminate* at the *surface* or at *boundaries*

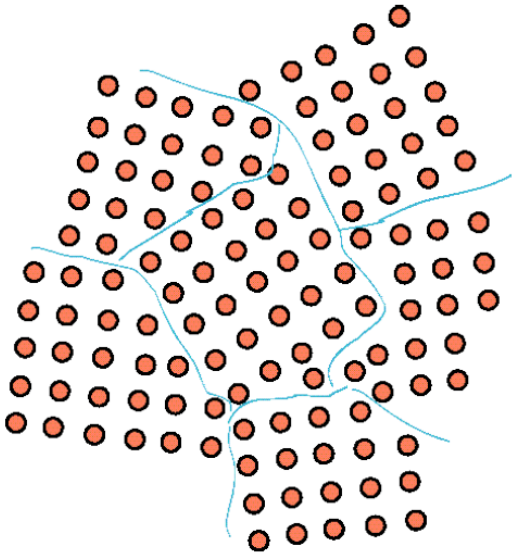
Surface Defects

External surface: Free surface

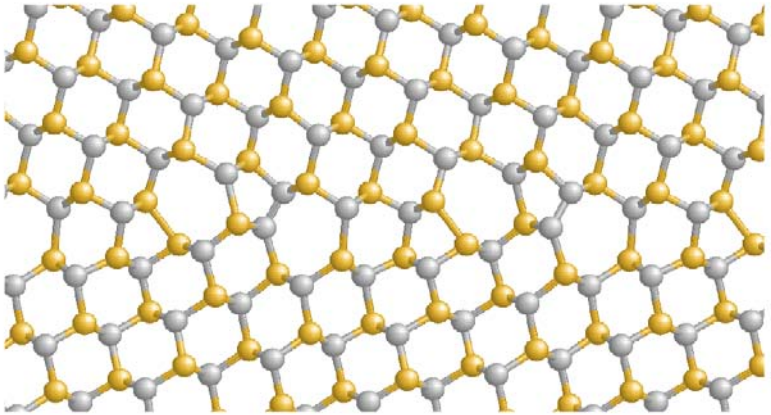




If bond are broken over an area A then two free surfaces of a total area 2A is created



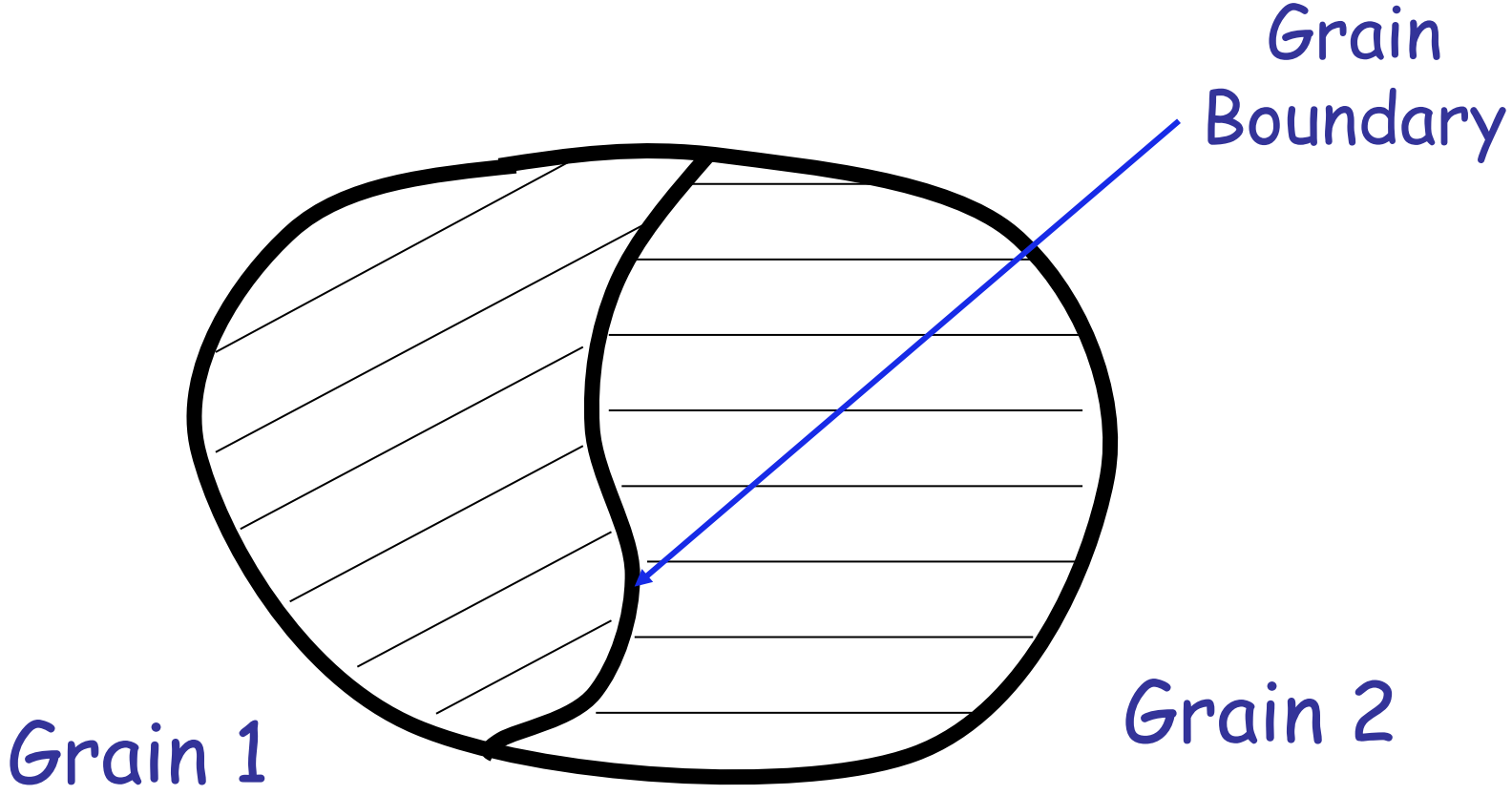
45.98° tilt grain boundary in SiC. A projection along the <110> direction is shown



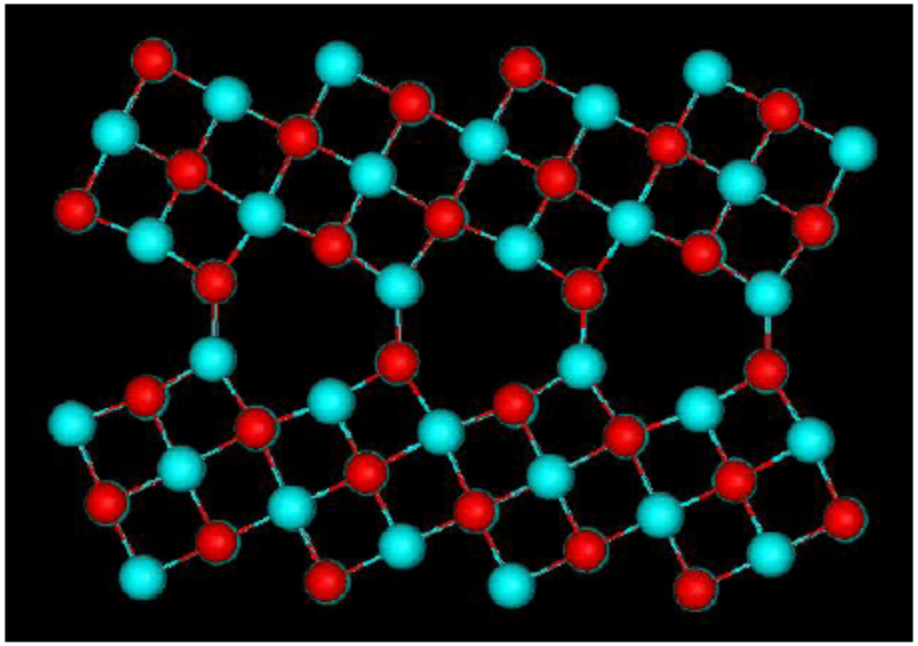
http://www.eng.utah.edu/~lzang/images/lecture-6-grain-boundary-displocation-defects-vancancy.pdf

- A **grain boundary** is the interface between two grains in a polycrystalline material
- they tend to decrease the electrical and thermal conductivity of the material

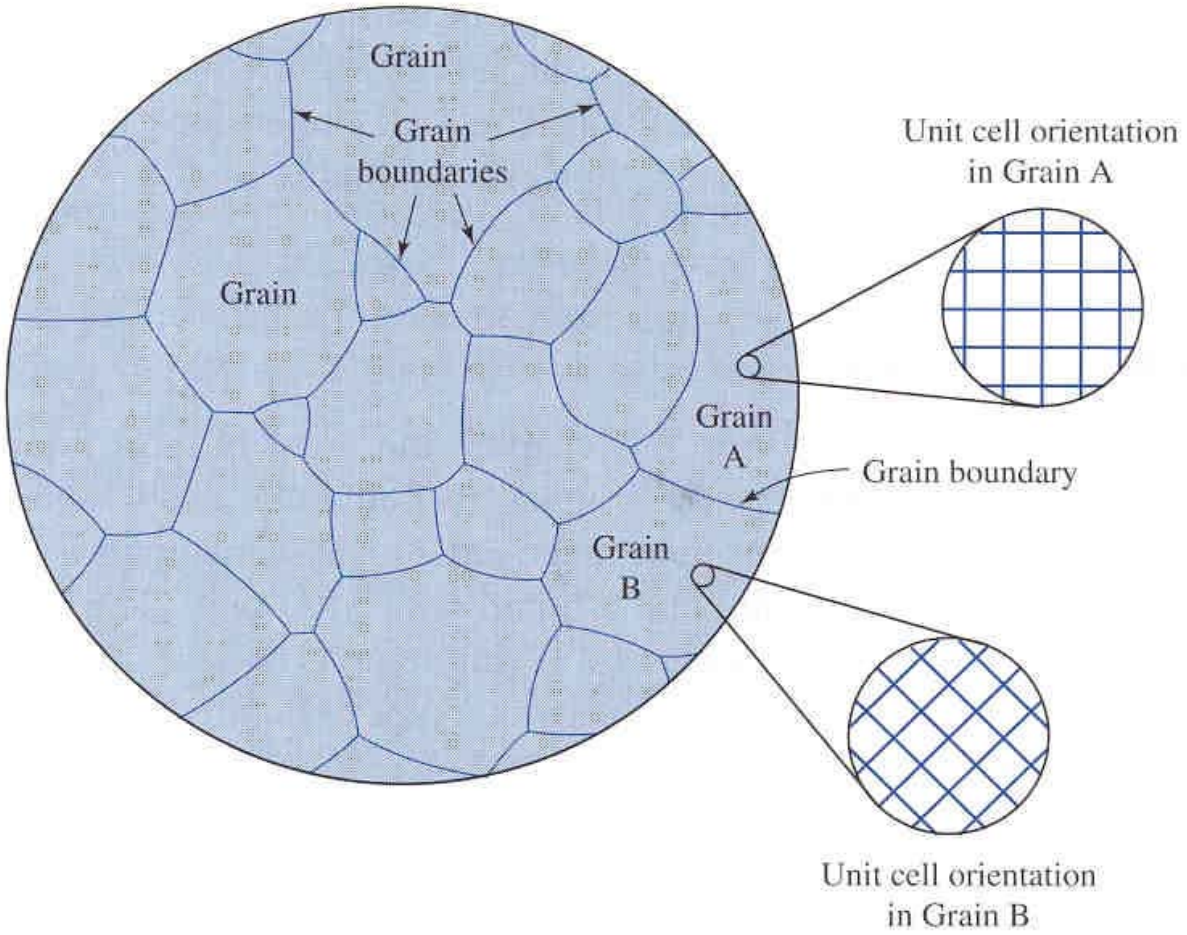
Internal surface: grain boundary

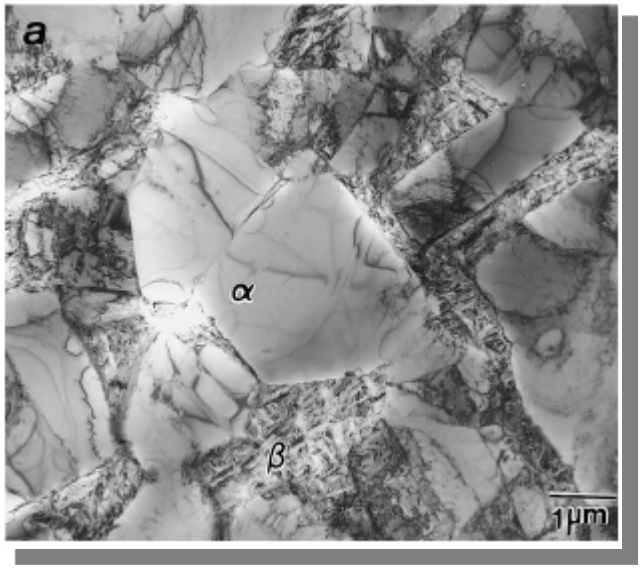


A grain boundary is a boundary between two regions of identical crystal structure but different orientation

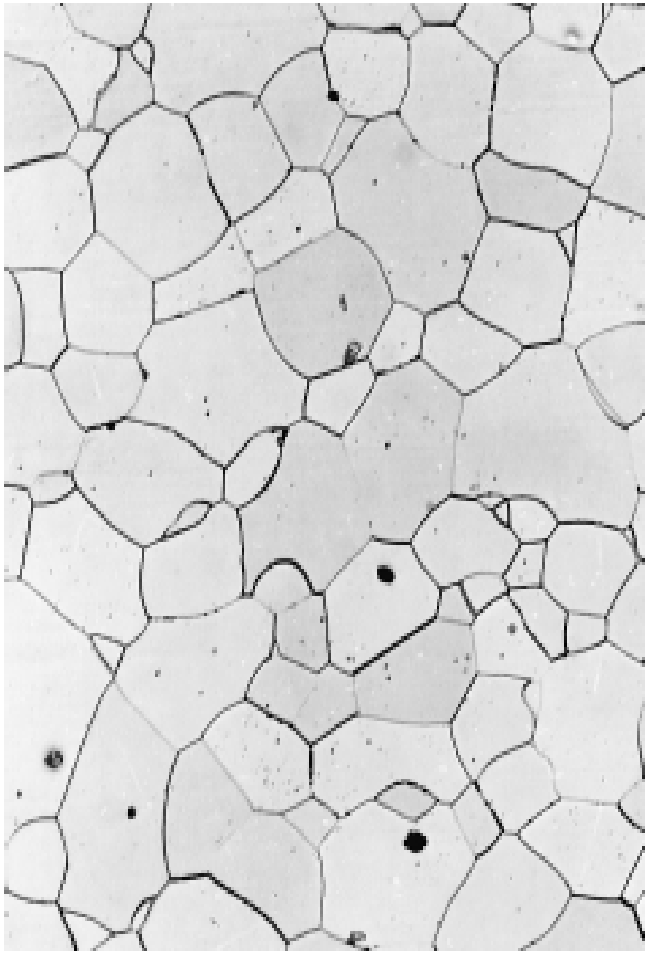


Can sometimes represent a grain boundary as a line of edge dislocations.





http://docplayer.info/104684-Metalurgi-fisik-sifat-mekanik-dan-struktur-mikro-10-24-2010-anrinal-itp.html



Photomicrograph of an iron chromium alloy. 100X.

http://docplayer.info/104684-Metalurgi-fisik-sifat-mekanik-dan-struktur-mikro-10-24-2010-anrinal-itp.html

galvanized surface with cristallites of zinc

http://web.utk.edu/~prack/mse201/Chapter%207%20Dislocations%20.pdf

High and low angle boundaries

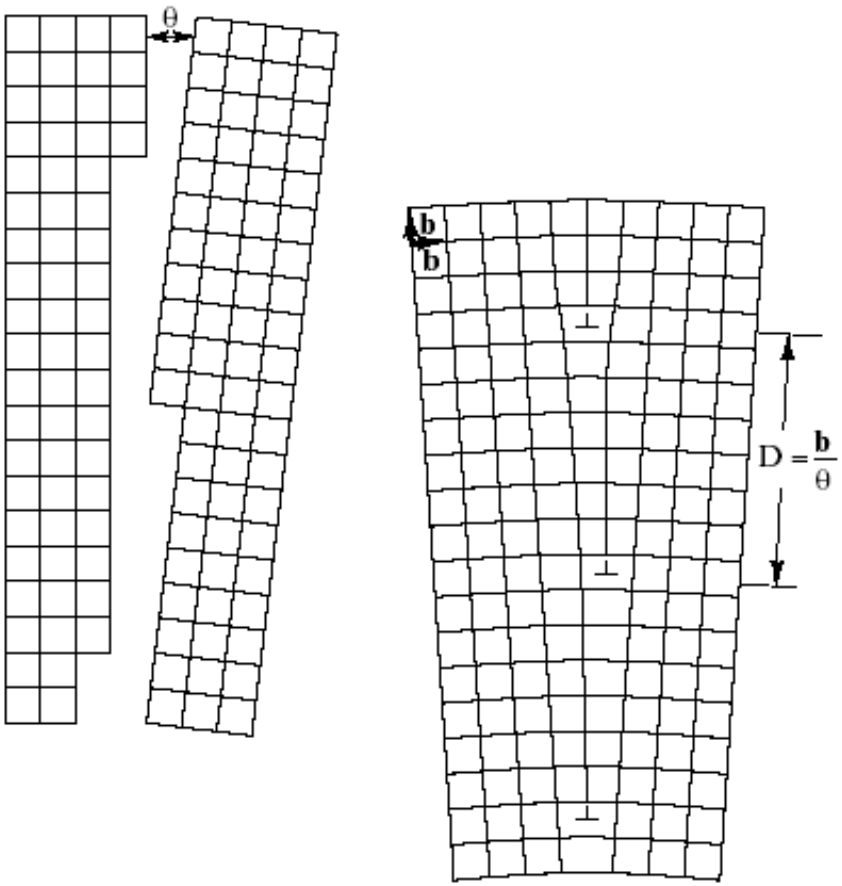
It is convenient to separate grain boundaries by the extent of the mis-orientation between the two grains.

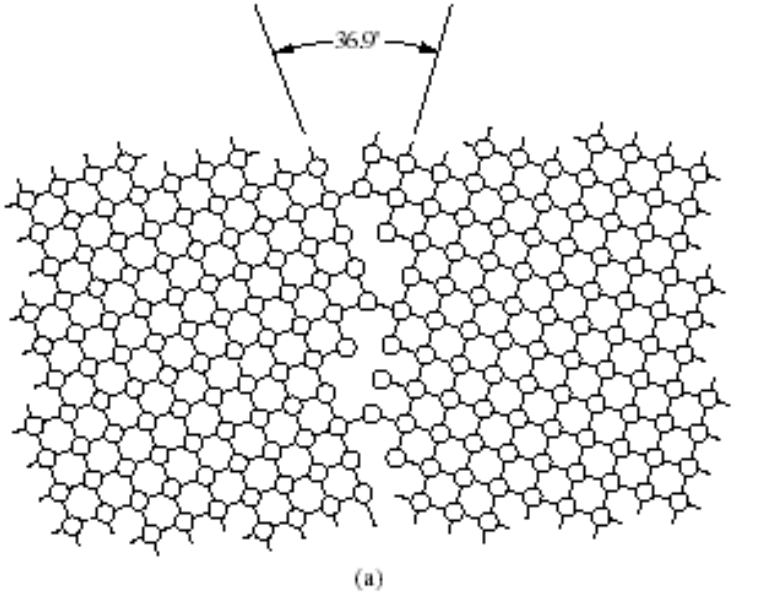
•*low angle grain boundaries* (LAGBs) are those with a misorientation less than about 11 degrees.

• *high angle grain boundaries* (HAGBs) whose misorientation is greater than about 11 degrees

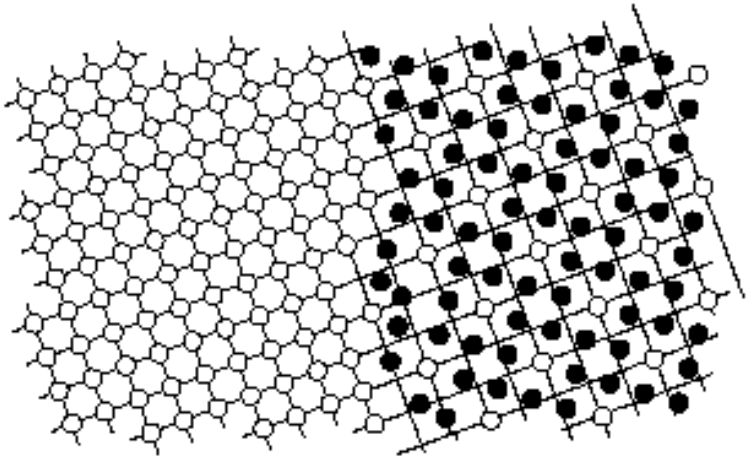
High angle boundary

Low angle boundary





(a)



(b)

Grain Boundary: tilt and twist

One grain orientation can be obtained by rotation of another grain across the grain boundary about an **axis** through an angle

If the axis of rotation lies in the boundary plane it is called tilt boundary

If the angle of rotation is perpendicular to the boundary plane it is called a

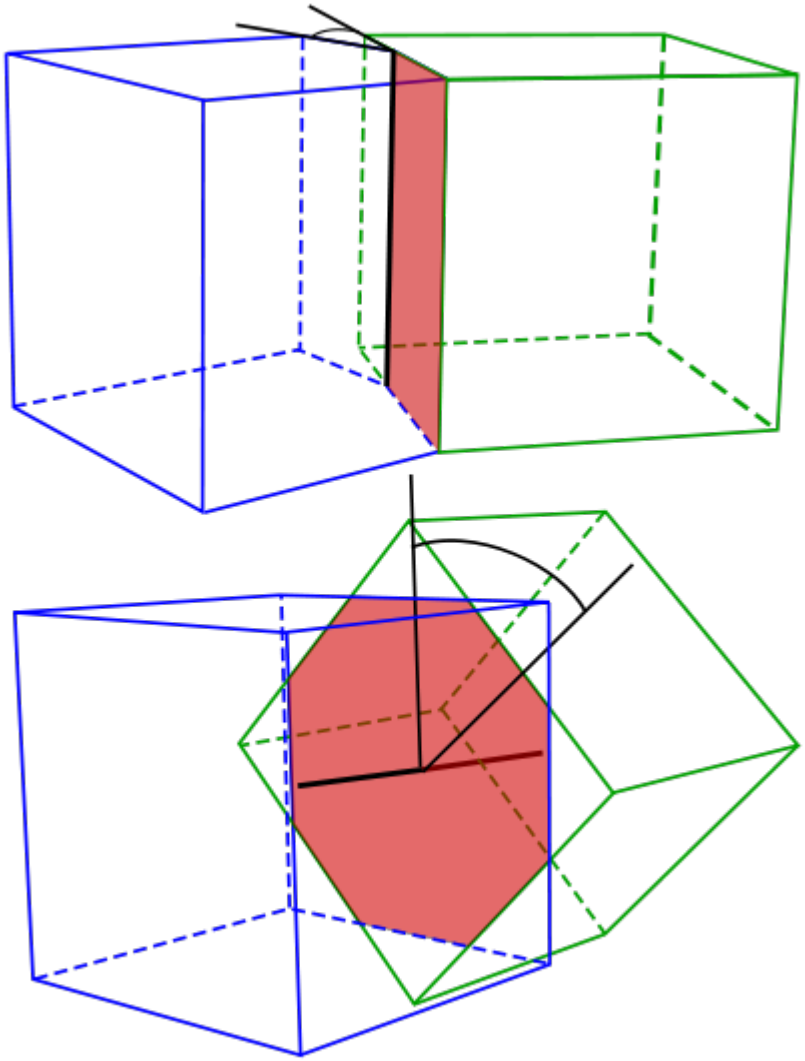
twist boundary

The most simple boundary is that of a tilt boundary where the rotation axis is parallel to the boundary plane. This boundary can be conceived as forming from a single, contiguous crystallite or grain which is gradually bent by some external force. The energy associated with the elastic bending of the lattice can be reduced by inserting a dislocation, which is essentially a half-plane of atoms that act like a wedge, that creates a permanent misorientation between the two sides. As the grain is bent further, more and more dislocations must be introduced to accommodate the deformation resulting in a growing wall of dislocations - a low-angle boundary. The grain can now be considered to have split into two sub-grains of related crystallography but notably different orientations.

An alternative is a twist boundary where the misorientation occurs around an axis that is perpendicular to the boundary plane

This type of boundary incorporates two sets of screw dislocations.

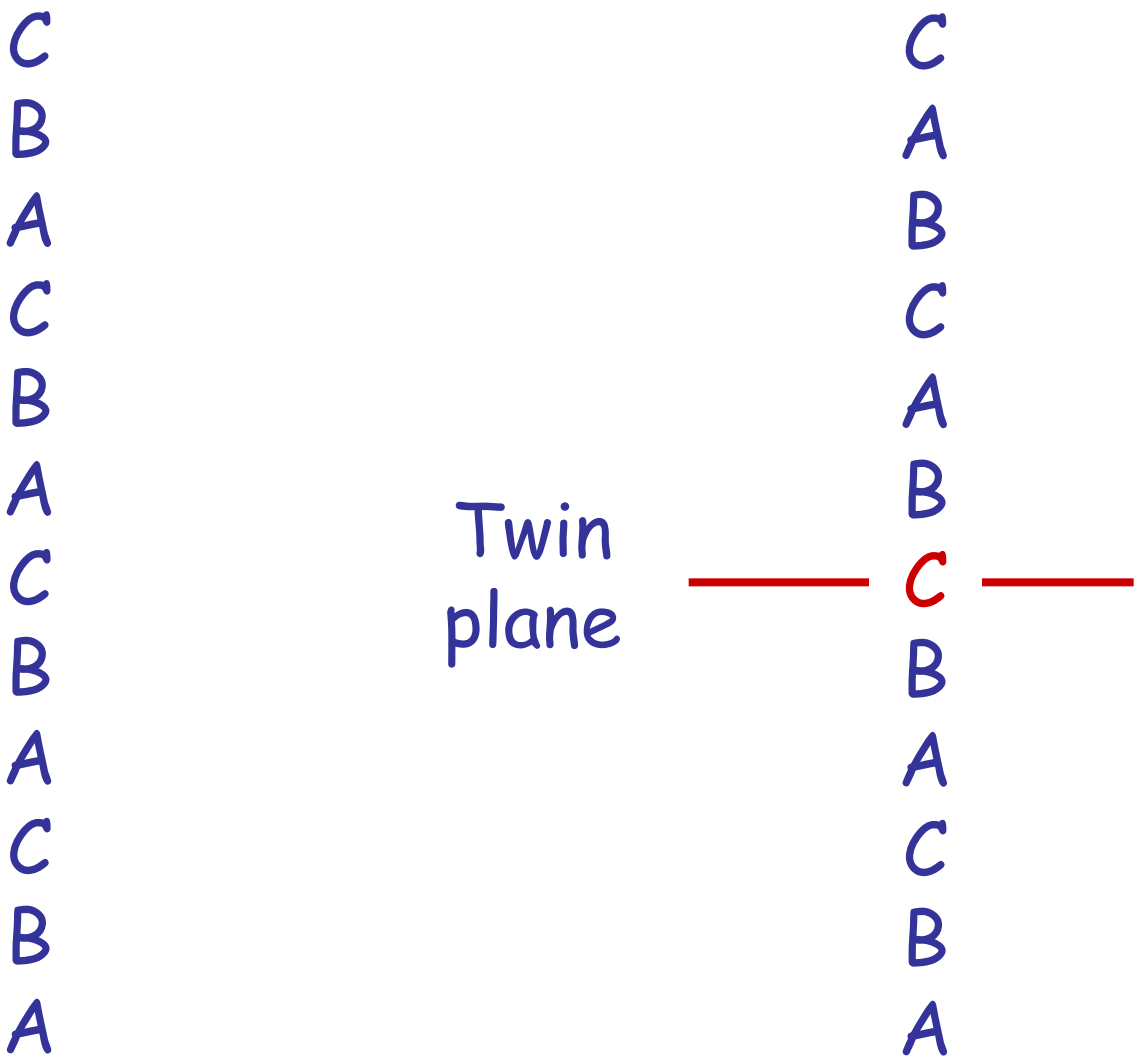
tilt boundary

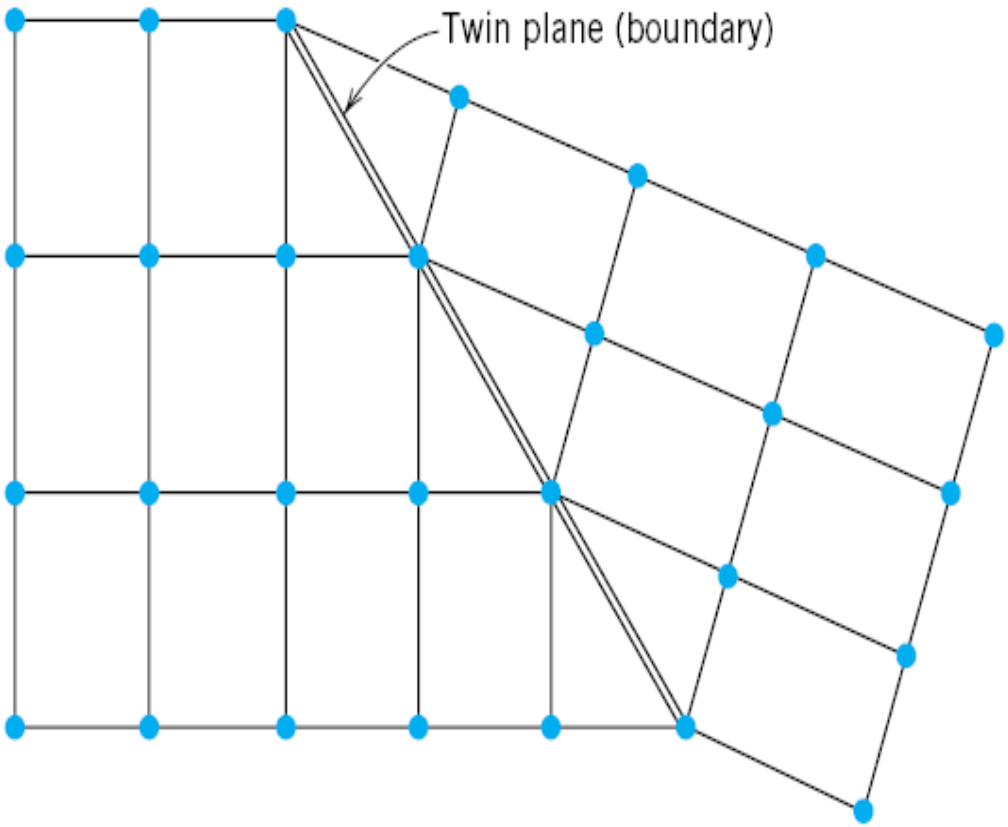


twist boundary

https://en.wikipedia.org/wiki/Grain_boundary

Twin Plane

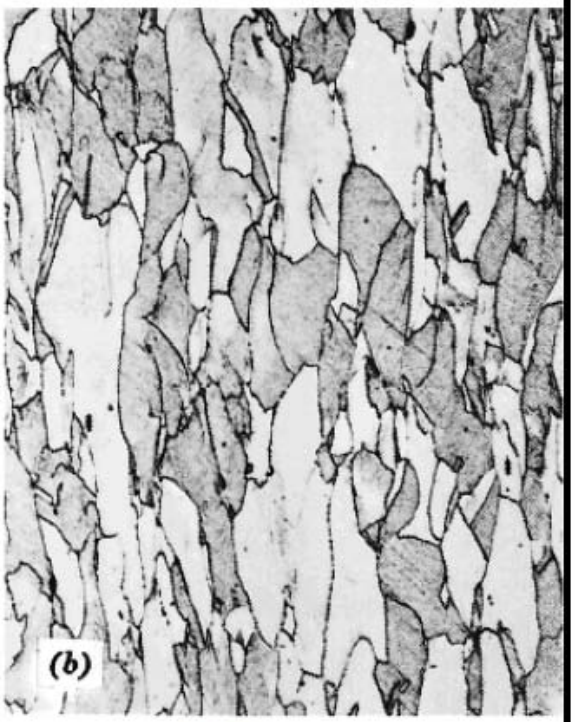



Twin plane (boundary)

Plastic Deformation of Polycrystalline Materials

Larger plastic deformation corresponds to elongation of grains along direction of applied stress.

Before



After

http://web.utk.edu/~prack/mse201/Chapter%207%20Dislocations%20.pdf

- Dislocations cannot easily cross grain boundaries because of changes in direction of slip plane and disorder at grain boundary
- **As a result, polycrystalline metals are stronger than single crystals** (the exception is the perfect single crystal without any defects, as in whiskers)

http://web.utk.edu/~prack/mse201/Chapter%207%20Dislocations%20.pdf

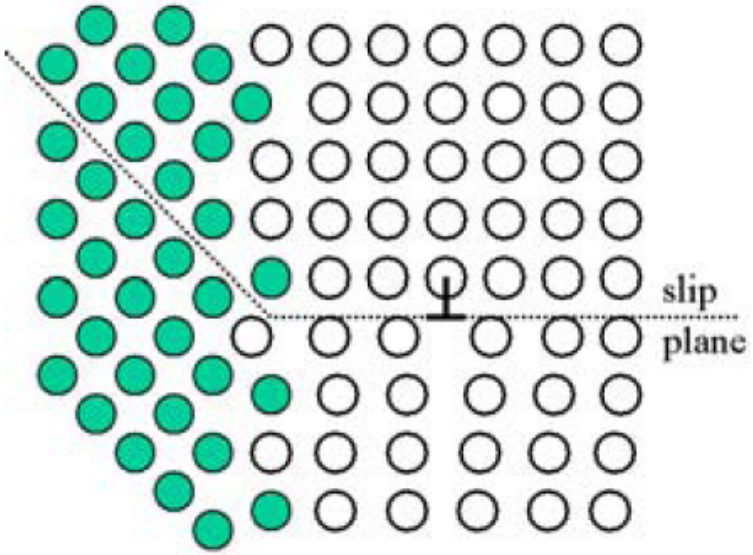
The ability of a metal to deform depends on the ability of dislocations to move

Restricting dislocation motion makes the material stronger

Mechanisms of strengthening in single-phase metals:

- grain-size reduction
- solid-solution alloying
- strain hardening

http://web.utk.edu/~prack/mse201/Chapter%207%20Dislocations%20.pdf



Grain boundary barrier to dislocation motion: slip plane discontinues or change orientation.

Small angle grain boundaries are not very effective in blocking dislocations.

High-angle grain boundaries block slip and increase strength of the material. A stress concentration at end of a slip plane may trigger new dislocations in an adjacent grain.

Alloys are usually stronger than pure metals of the solvent.

Interstitial or substitutional impurities in a solution cause lattice strain. As a result, these impurities interact with dislocation strain fields and **hinder dislocation motion**.

Impurities tend to diffuse and **segregate around the dislocation core** to find atomic sites more suited to their radii. This reduces the overall strain energy and "anchor" the dislocation.

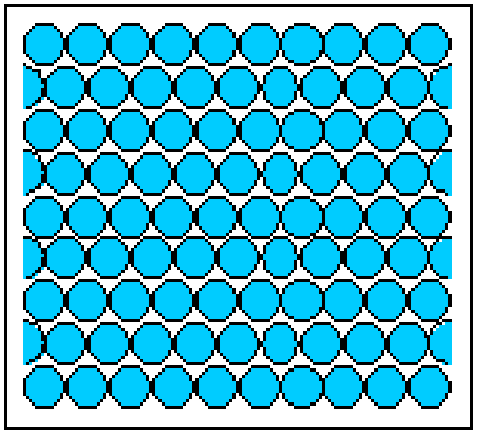
Motion of the dislocation core away from the impurities moves it to a region of lattice where the atomic strains are greater (i.e. the dislocation strains are no longer compensated by the impurity atoms).

http://web.utk.edu/~prack/mse201/Chapter%207%20Dislocations%20.pdf

Ductile metals become stronger when they are deformed plastically at temperatures well below the melting point.

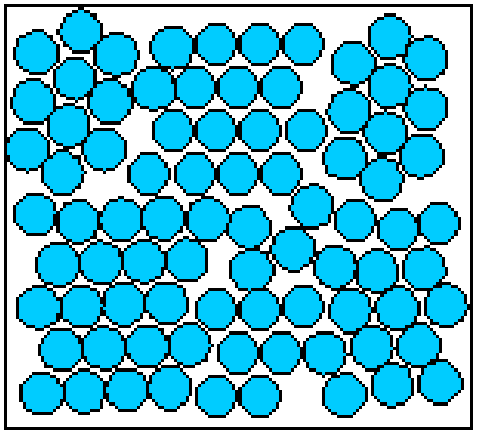
The reason for strain hardening is the increase of dislocation density with plastic deformation. The average distance between dislocations decreases and dislocations start blocking the motion of each other.

http://web.utk.edu/~prack/mse201/Chapter%207%20Dislocations%20.pdf



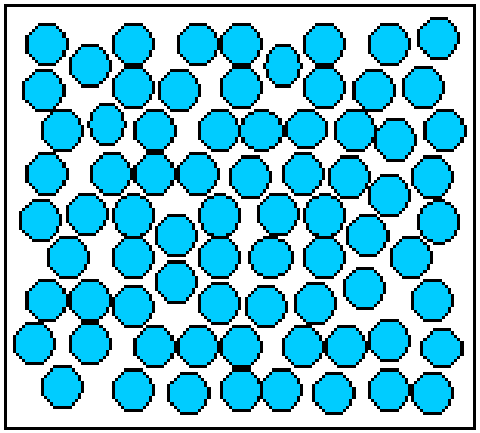
Single crystal

Periodic across the whole volume.



Polycrystal

Periodic across each grain.



Amorphous solid

Not periodic.

http://poozacreations.blogspot.ro/2012/03/structure-of-solids.html

Observation of Grain Structure

FIGURE 4.10 High-purity polycrystalline lead ingot in which the individual grains may be discerned.

- *Macrostructure* can be observed with naked eye
- coarse grains can be revealed this way (e.g. Al streetlight posts e.g. zinc galvanized garbage cans
- *microstructure* is when the grains can only be observed with a microscope → *microscopy*
- imaged using a camera for archiving

  → *photomicrograph*

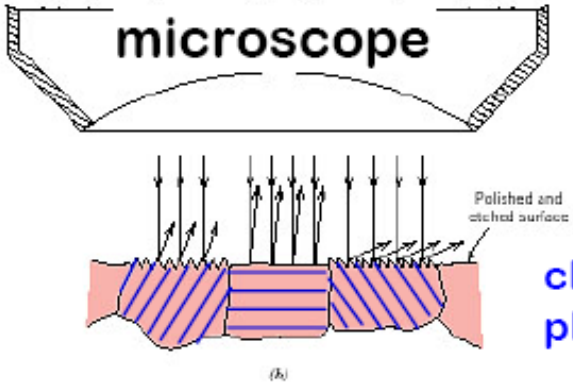
Microscopic Examination

- Crystallites (grains) and grain boundaries vary considerably in size.
- Can be quite large
  - ex: Large single crystal of quartz or diamond or Si
  - ex: Aluminum garbage can - see the individual grains
- Can be quite small (mm to nm)
  necessary to observe with a microscope,
  even a TEM. “microstructure”, “nanostructure”

see http://academic.uprm.edu/pcaceres/Courses/MatEng/MSE4-1.pdf

Optical microscopy

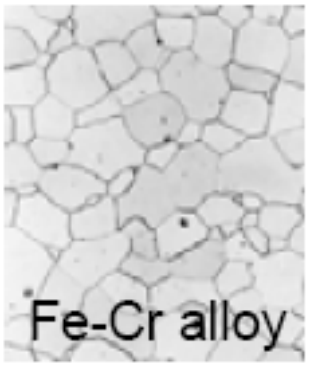
- Useful up to 2000X magnification.
- Polishing removes surface features (e.g., scratches)
- Etching changes reflectance, depending on crystal orientation.



close-packed planes

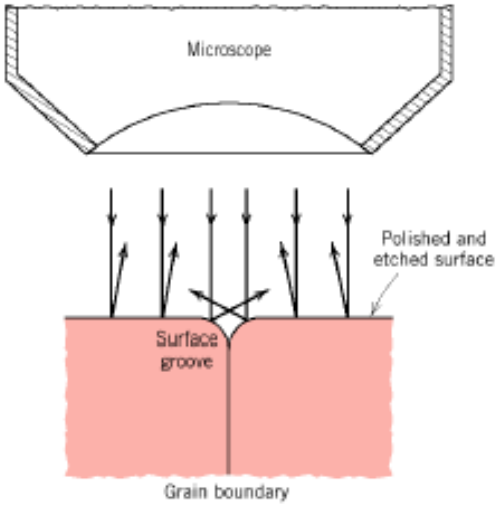
micrograph of Brass (Cu and Zn)

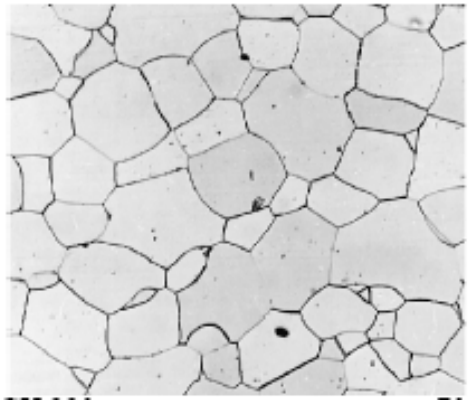
0.75mm



http://academic.uprm.edu/pcaceres/Courses/MatEng/MSE4-1.pdf

Sample Preparation for Microscopy





- Preparation requires meticulous *grinding and polishing* of the surface
- the microstructure is revealed by attack using *etchants* (chemical reagents
  - preferential attack of grain boundaries
- effect is that these features scatter the incident light and create optical contrast

http://academic.uprm.edu/pcaceres/Courses/MatEng/MSE4-1.pdf

Microscopy

Optical resolution ca. 10^{-7} m = 0.1 μm = 100 nm

For higher resolution need higher frequency

X-Rays? Difficult to focus.

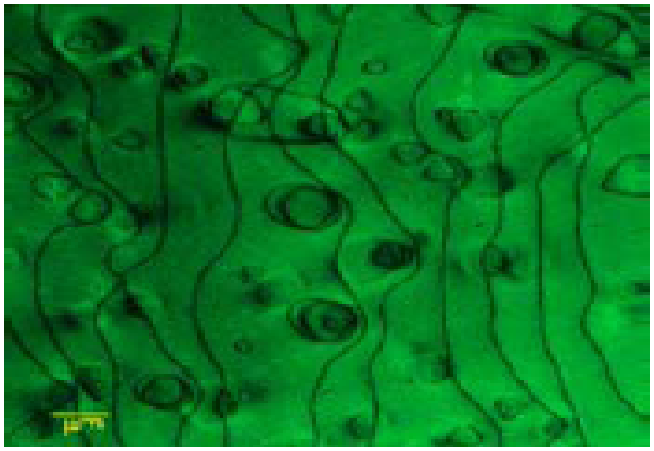
Electrons (SEM, TEM, STEM)

- wavelengths ca. 3 pm (0.003 nm)
  (Magnification - 1,000,000X)
- Atomic resolution possible
- Electron beam focused by magnetic lenses.

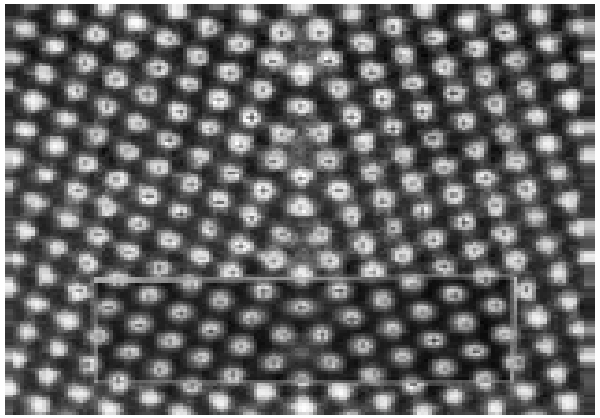
Scanning Probe Microscopies (STM, AFM, …)

http://academic.uprm.edu/pcaceres/Courses/MatEng/MSE4-1.pdf

Electron Microscopy



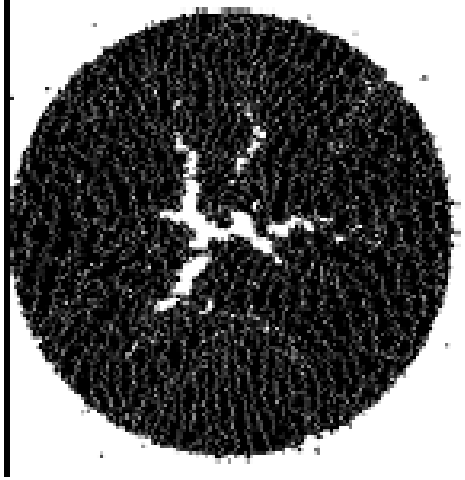
Dislocations in Nickel (the dark lines and loops), transmission electron microscopy image, Manchester Materials Science Center.



High-resolution Transmission Electron Microscope image of a tilt grain boundary in aluminum, Sandia National Lab.

Bulk or Volume Defects

- **Pores** - can greatly affect optical, thermal, mechanical properties
- **Cracks** - can greatly affect mechanical properties
- **Foreign inclusions** - can greatly affect electrical, mechanical, optical properties



A cluster of microcracks in a melanin granule irradiated by a short laser pulse. Computer simulation by L. V. Zhigilei and B. J. Garrison.

http://web.utk.edu/~prack/mse201/Chapter%204%20Defects.pdf

Conclusions

- Point, line and area defects arise in solids.
- The number and type of defects depend on several factors (e.g. the concentration of vacancied can be controled by temperature).
- The properties of the materials are affected by defects (e.g. defects control mechanical , electrical, optical properties…)
- Defects can be wanted or unwanted depending of the specific application.